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**Developing an MNA Modeling Tool based on RT3D: 3
Reports**

**Natural and Enhanced Attenuation of Chlorinated Solvents
Using RT3D**

**RT3D Reaction Modules for Natural and Enhanced
Attenuation of Chloroethanes, Chloroethenes,
Chloromethanes, and Daughter Products**

rtFlux: RT3D Flux Plane Utility

**(A Research Study of the Monitored Natural Attenuation/Enhanced
Attenuation for Chlorinated Solvents Technology Alternative Project)**

October 11, 2006

Washington Savannah River Company
Savannah River Site
Aiken, SC 29808

Prepared for the U.S. Department of Energy
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SR18500



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Executive Summary

Integral to the acceptance of MNA and EA as part of a remediation system is documenting the sustainability of the attenuation mechanisms. As many sites are located in complex hydrogeologic settings, documentation of sustainability will require the use of complex models that have the capabilities to mathematically represent the various attenuation mechanisms. To address this need a team of researchers developed specific reaction modules for complex chlorinated solvent reactions that occur in the subsurface. These reaction modules support the RT3D model.

Introduction

Over the past three decades, much progress has been made in the remediation of soil and groundwater contaminated by chlorinated solvents. Yet these pervasive contaminants continue to present a significant challenge to the U.S. Department of Energy (DOE), other federal agencies, and other public and private organizations. The physical and chemical properties of chlorinated solvents make it difficult to rapidly reach the low concentrations typically set as regulatory limits. These technical challenges often result in high costs and long remediation time frames. In 2003, the DOE through the Office of Environmental Management funded a science-based technical project that uses the U.S. Environmental Protection Agency's technical protocol (EPA, 1998) and directives (EPA, 1999) on Monitored Natural Attenuation (MNA) as the foundation on

which to introduce supporting concepts and new scientific developments that will support remediation of chlorinated solvents based on natural attenuation processes. This project supports the direction in which many site owners want to move to complete the remediation of their site(s), that being to complete the active treatment portion of the remedial effort and transition into MNA.

The overarching objective of the effort was to examine environmental remedies that are based on natural processes – remedies such as Monitored Natural Attenuation (MNA) or Enhanced Attenuation (EA). The research program did identify several specific opportunities for advances based on: 1) mass balance as the central framework for attenuation based remedies, 2) scientific advancements and achievements during the past ten years, 3) regulatory and policy development and real-world experience using MNA, and 4) exploration of various ideas for integrating attenuation remedies into a systematic set of “combined remedies” for contaminated sites. These opportunities are summarized herein and are addressed in more detail in referenced project documents and journal articles, as well as in the technical and regulatory documents being developed within the ITRC.

Three topic areas were identified to facilitate development during this project. Each of these topic areas, 1) mass balance, 2) enhanced attenuation (EA), and 3) innovative characterization and monitoring, was explored in terms of policy, basic and applied research, and the results integrated into a technical approach. Each of these topics is documented in stand alone reports, WSRC-STI-2006-00082, WSRC-STI-2006-00083, and WSRC-STI-2006-00084, respectively. In brief, the mass balance efforts are

examining methods and tools to allow a site to be evaluated in terms of a system where the inputs, or loading, are compared to the attenuation and destruction mechanisms and outputs from the system to assess if a plume is growing, stable or shrinking. A key in the mass balance is accounting for the key attenuation processes in the system and determining their rates. EA is an emerging concept that is recognized as a transition step between traditional treatments and MNA. EA facilitates and enables natural attenuation processes to occur in a sustainable manner to allow transition from the primary treatment to MNA. EA technologies are designed to either boost the level of the natural attenuation processes or decrease the loading of contaminants to the system for a period of time sufficient to allow the remedial goals to be met over the long-term. For characterization and monitoring, a phased approach based on documenting the site specific mass balance was developed. Tools and techniques to support the approach included direct measures of the biological processes and various tools to support cost-effective long-term monitoring of systems where the natural attenuation processes are the main treatment remedies. The effort revealed opportunities for integrating attenuation mechanisms into a systematic set of “combined remedies” for contaminated sites.

An important portion of this project was a suite of 14 research studies that supported the development of the three topic areas. A research study could support one or more of these three topic areas, with one area identified as the primary target. One of the most important development targets is related to modeling tools to support MNA and EA decisions. In recognition of the varying conditions and complexity that occur at real-world facilities and the need for a site specific approach, the portfolio of modeling and decision-making research projects was selected to be diverse. The four associated projects were specifically selected to include an MNA/EA screening system, simplified analytical models, key modular developments for more complex numerical models, and decision support tools. By investing in this breadth of projects, the effort supports a philosophy of matching the evaluation tool(s) to the subject site and the research provided concrete and usable products.

The following reports document the results of the development of reaction modules that will support natural and enhanced attenuation of chlorinated solvents for the RT3D three-dimensional reactive transport model. This effort was led by Michael Truex and Christian Johnson of Pacific Northwest National Laboratory. This study supports the topic area(s) of mass balance and Enhanced Attenuation with characterization and monitoring being a secondary development area. The objective of the study was to develop specific reaction modules for complex chlorinated solvent reactions that occur in the subsurface. The resulting product is three reports. The first, Attachment 1, *Natural and Enhanced Attenuation of Chlorinated Solvents Using RT3D*, identifies when various types of models are appropriate, the attenuation processes available for simulation in RT3D, a discussion of potential dechlorination reactions, and the general approach for using the RT3D reaction modules that support MNA. The second product, Attachment 2, *RT3D Reaction Modules for Natural and Enhanced Attenuation for Chloroethanes, Chloroethenes, Chloromethanes, and Daughter Products*, provides the details of the reaction kinetics, data input requirements, and an example for each of the new reaction modules. The third product, Attachment 3, *rtFLux: RT3D Flux Plane Utility*, presents a

software utility that provides the results in terms of mass flux. In recognition of the importance of mass balance to MNA and EA decisions, this postprocessor that runs in excel was developed to allow modeling results from RT3D to be presented as cross sections that graphically depict the “mass flux” in different parts of the subsurface system. This type of tool is an example of a simple yet powerful technique to improve conceptual understanding of a plume and to target and optimize any remediation – whether the goal is primary source treatment/removal or EA.

As more site owners consider natural attenuation based remedies as part of their treatment plans, incorporating reaction modules representative of the dechlorination reactions that occur to chlorinated solvents in the subsurface into fate and transport models will increase their usefulness in decision-making. Typically high-end, multi-dimensional, numerical models such as RT3D are chosen because the unit being modeled has great complexity and/or there is a need to predict future conditions. By incorporating new modules that simulate dechlorination reactions along with the existing non-biological attenuation processes supports the user in performing a more complete mass balance calculation. This is true whether evaluating a site for MNA or Enhanced Attenuation (EA) treatment, as EA treatments are designed and constructed to promote natural attenuation processes being sustainable for the time period needed to meet the overall treatment objectives.

This research effort provides added capabilities to an already valuable tool in the modeling toolbox. Potential users are encouraged to consider their site characteristics when selecting the model of choice for their site. Figure 1, in the attached *Natural and Enhanced Attenuation of Chlorinated Solvents Using RT3D* document, or the *Scenarios Evaluation Tool for Chlorinated Solvent MNA* (Truex et al., 2006) both provide guidance on model selection based on site characteristics.

References for Introduction

EPA, 1998. *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater*, EPA/600/R-98/128. Washington DC. September 1998.

EPA, 1999. *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action and Underground Storage Tank Sites*, OSWER Directive 9200.4-17P. Washington DC. April 21, 1999.

WSRC-STI-2006-00082, 2006. *Mass Balance: A Key to Advancing Monitored and Enhanced Attenuation for Chlorinated Solvents*. Washington Savannah River Company, Aiken, SC, 29808. June 2006. Available at www.osti.gov.

WSRC-STI-2006-00083, 2006. *Enhanced Attenuation: A Reference Guide on Approaches to Increase the Natural Treatment Capacity of a System*, Revision 1. Washington Savannah River Company, Aiken, SC, 29808. August 2006. Available at www.osti.gov.

WSRC-STI-2006-00084, 2006. *Characterization and Monitoring of Natural Attenuation of Chlorinated Solvents in Ground Water: A Systems Approach*, Revision 1. Washington Savannah River Company, Aiken, SC, 29808. August 2006. Available at www.osti.gov.

Attachment 1:

**Natural and Enhanced Attenuation of Chlorinated Solvents Using
RT3D**



**Pacific Northwest
National Laboratory**

Operated by Battelle for the
U.S. Department of Energy

Natural and Enhanced Attenuation of Chlorinated Solvents Using RT3D

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T.P. Clement

July 2006



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Natural and Enhanced Attenuation of Chlorinated Solvents Using RT3D

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July 2006

Prepared for
the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Summary

RT3D (Reactive Transport in 3-Dimensions) is a reactive transport code that can be applied to model solute fate and transport for many different purposes. This document specifically addresses application of RT3D for modelling related to evaluation and implementation of Monitored Natural Attenuation (MNA). Selection of MNA as a remedy requires an evaluation process to demonstrate that MNA will meet the remediation goals. The United States Environmental Protection Agency, through the Office of Solid Waste and Emergency Response (OSWER) Directive 9200.4-17P, provides the regulatory context for the evaluation and implementation of MNA. In a complementary fashion, the context for using fate and transport modelling as part of MNA evaluation is described in the EPA's technical protocol for chlorinated solvent MNA, the *Scenarios Evaluation Tool for Chlorinated Solvent MNA*, and in this document. The intent of this document is to describe 1) the context for applying RT3D for chlorinated solvent MNA, 2) the attenuation processes represented in RT3D, 3) dechlorination reactions that may occur, and 4) the general approach for using RT3D reaction modules (including a summary of the RT3D reaction modules that are available) to model fate and transport of chlorinated solvents as part of MNA (potentially in combination with selected types of active remediation).

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This document is a product of the Monitored Natural Attenuation / Enhanced Attenuation for Chlorinated Solvents Technology Alternative Project (MNA/EA Alternative Project). The MNA/EA Alternative Project was sponsored by the U.S. Department of Energy (DOE) Office of Cleanup Technologies and administered by the U.S. Department of Energy Savannah River (SR) Operations Office. The authors appreciate the guidance and support of Claire H. Sink of DOE Headquarters and Karen M. Adams of DOE SR. The authors thank Brian Looney and Karen Vangelas of Savannah River National Laboratory and the MNA/EA Alternative Project Technical Working Group for their review and feedback on the work documented here.

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1.0 Introduction

RT3D (Reactive Transport in 3-Dimensions) [Clement, 1997; Clement et al., 1998, Clement and Johnson, 2002] is a reactive transport code that can be applied to model solute fate and transport for many different purposes. This document specifically addresses application of RT3D for modelling related to evaluation and implementation of Monitored Natural Attenuation (MNA). Selection of MNA as a remedy requires an evaluation process to demonstrate that MNA will meet the remediation goals. The United States Environmental Protection Agency (U.S. EPA), through the Office of Solid Waste and Emergency Response (OSWER) Directive 9200.4-17P [U.S. EPA, 1999a], provides the regulatory context for the evaluation and implementation of MNA. In a complementary fashion, the context for using fate and transport modelling as part of MNA evaluation is described in the EPA's technical protocol for chlorinated solvent MNA [U.S. EPA, 1998], the *Scenarios Evaluation Tool for Chlorinated Solvent MNA* [Truex et al., 2006], and in this document. The intent of this document is to describe 1) the context for applying RT3D for chlorinated solvent MNA, 2) the attenuation processes represented in RT3D, 3) dechlorination reactions that may occur, and 4) the general approach for using RT3D reaction modules (including a summary of the RT3D reaction modules that are available) to model fate and transport of chlorinated solvents as part of MNA or for combinations of MNA and selected types of active remediation.

This document provides the following information related to applying RT3D for chlorinated solvent MNA. Section 2.0 is an overview of MNA. In Section 3.0, an overview of reactive transport modelling for MNA is presented. Section 4.0 provides a discussion of specific roles for modelling as part of MNA evaluation and implementation. A description of how RT3D models reactive transport is presented in Section 5.0. In Section 6.0, the specific reactions for the chlorinated species that are included in the RT3D reaction modules for MNA are described. Section 7.0 discusses how to select the RT3D reaction module based on contaminants and the type of modelling that is required at the site. Section 8.0 describes the process for applying a reaction module for fate and transport modelling.

2.0 Overview of MNA

Monitored Natural Attenuation is an environmental management strategy that relies on a variety of attenuation processes to degrade or immobilize contaminants and is implemented at appropriate sites by demonstrating that contaminant plumes have low risk and are either stable or shrinking. The U.S. EPA “*Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites*” OSWER Directive [U.S. EPA, 1999a], hereafter referred to as the “OSWER MNA Directive,” is the primary document describing the regulatory context for MNA. The natural attenuation (NA) processes recognized in the OSWER MNA Directive are delineated in the following quotation [U.S. EPA, 1999a, page 3].

The “natural attenuation processes” that are at work in such a remediation approach [MNA] include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil or groundwater. These in-situ processes include biodegradation; dispersion; dilution; sorption; volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants.

The OSWER MNA Directive outlines a three-tiered approach that has generally been used for evaluating the suitability of MNA as a remedy. This approach includes use of:

1. Historical groundwater and/or soil chemistry data that demonstrate a clear and meaningful trend of decreasing contaminant mass and/or concentration over time at appropriate monitoring or sampling points. (In the case of a groundwater plume, decreasing concentrations should not be solely the result of plume migration. In the case of inorganic contaminants, the primary attenuating mechanism should also be understood.)
2. Hydrogeologic and geochemical data that can be used to demonstrate indirectly the type(s) of natural attenuation processes active at the site, and the rate at which such processes will reduce contaminant concentrations to required levels. (For example, characterization data may be used to quantify the rates of contaminant sorption, dilution, or volatilization, or to demonstrate and quantify the rates of biological degradation processes occurring at the site.)
3. Data from field or laboratory microcosm studies (conducted in or with actual contaminated site media) which directly demonstrate the occurrence of a particular natural attenuation process at the site and its ability to degrade the contaminants of concern (typically used to demonstrate biological degradation processes only).

Specific steps for determining whether MNA can meet remediation goals for chlorinated solvents are provided in the *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water* [U.S. EPA, 1998], referred to here as the “EPA MNA Protocol.”

Briefly, this protocol outlines data and analysis requirements that include 1) site characterization, 2) an initial screening assessment to verify that site conditions are consistent with the conditions needed for NA processes, 3) developing “lines of evidence” that NA is occurring, and 4) demonstrating (e.g., through fate and transport modelling) that NA is likely to mitigate plume migration and meet remediation goals. If MNA is selected as the remedy, it is implemented using a monitoring plan designed to verify that NA processes continue to attenuate the plume and that remediation goals are met over time.

The *Scenarios Evaluation Tool for Chlorinated Solvent MNA* [Truex et al., 2006] provides a framework that links the MNA evaluation and associated decision logic to key site characteristics and known natural attenuation phenomena. The approach is to take the wide spectrum of chlorinated solvent sites (e.g., different sources, hydrogeology, geochemistry, degradation process) and sort them into one of 13 different MNA scenarios. By applying a taxonomic system, users can determine which scenario best describes their plume (or a segment of their plume). Each scenario contains information about how to proceed with MNA evaluation for the type of plumes that fit within the scenario. The approach includes information to determine when numerical modelling may be needed as part of the MNA evaluation process.

MNA may be a viable single remedy for the site. However, if it is determined that MNA may not meet remediation goals, Enhanced Attenuation (EA) approaches may be considered. The EA approach is to use a remediation technology that is a sustainable enhancement to natural attenuation either through reduction of source flux (loading) to the plume or through enhancing the attenuation processes. More aggressive source control may also be necessary for sites where incremental enhancements alone are unlikely to be sufficient.

EA approaches can be categorized by the different zones to which they are applied: source zone (reduction of contaminant mass flux to plume); plume (enhanced attenuation processes); or discharge zone (enhanced attenuation processes). Within the source zone, enhancements can be applied as a hydraulic manipulation or as a passive source reduction. Within the plume and discharge zone, either biological (microbial or plant based) or abiotic (abiotic degradation, reactive barriers, sorption) attenuation processes can be enhanced. More detailed information about EA technologies is available in Early et al. [2006].

Source control actions include active remediation of the source area through biological or chemical remediation processes (e.g., bioremediation, thermal treatment, chemical oxidation, solvent flushing) or active containment approaches such as pump-and-treat. These actions are more active/aggressive source reduction and containment approaches, which may be needed for strong source areas that have a significant mass of contamination feeding the plume.

3.0 Overview of Reactive Transport Modelling for MNA

The concept of a mass balance between the loading and attenuation of contaminants in a groundwater system provides a framework for conceptualizing and documenting the relative stability of a contaminant plume. Thus, a mass balance concept has significant potential to support appropriate implementation of MNA or EA. For a mass balance to be useful in engineering practice, however, it is necessary to quantify it in practical ways that facilitate overall site remediation and which are consistent with existing regulatory guidance. Fate and transport modelling can be used for implementing this type of plume analysis and providing a technical basis for evaluating MNA as a remedy when simpler evaluations are not suitable.

The type of model applied at a specific site is dependent on the site conditions and the intended use of the model. The discussion here is limited to models for solute transport under saturated conditions. In addition to the conceptual model, which is a necessary part of any site evaluation, two basic levels of models that are relevant to MNA modelling are available. Analytical models (e.g., BIOCHLOR [U.S. EPA, 1999b] or ART3D [Quezada et al., 2003]) are capable of solving the general transport equation with specific limitations. Three-dimensional multi-species reactive transport numerical models, such as RT3D, discretize the transport equation and iteratively solve it within a defined numerical domain. As such, RT3D allows for more detailed configuration of the model domain to more closely match site features. Selection of the appropriate level of model for a specific site is dependent on the site conditions and configuration-related differences between analytical models and numerical models. Table 1 provides a brief overview of considerations for selecting the primary type of modelling analysis based on site properties, in particular based on whether the geochemistry and hydrology of the site readily supports a relatively simple description of attenuation and transport processes or whether the geochemistry and hydrology are complex. Other considerations for model selection are discussed below.

BIOCHLOR [U.S. EPA, 1999b] and ART3D [Quezada et al., 2003 and 2004; Clement, 2001] are analytical models that have been established specifically for use in modelling MNA. For analytical models, the solution technique typically requires assumptions of uniform hydraulic properties throughout the domain, uniform steady-state groundwater flow (in some case limited to one-dimensional advection), simple boundary conditions, simple source geometry, first-order contaminant transformation with rates constant within a defined area (in some cases for a single decay pathway), and uniform linear equilibrium partitioning. Analytical models can be useful in providing estimates of contaminant migration for plumes where these assumptions can be technically supported based on the site conditions. For instance, consider a plume with a well-defined contaminant source of TCE within a relatively homogeneous, thin aquifer that is bounded by aquitards or by an aquitard and the water table and where the aquifer has relatively constant methanogenic conditions throughout the plume. In this case, the assumptions required for use of an analytical model are appropriate.

Table 1. Considerations for Selecting a Modelling Approach Based on Site Properties

Modelling Approach	Sites with supportive geochemical / hydrologic conditions		Sites with hydrologic and / or geochemical complexity / challenges		
	Simple site with stable or shrinking plume	Plume stability & geochemical footprints uncertain	Documented plume growth or outcrop or perturbed – may be stable in the future	Geochemical conditions uncertain and/or complex hydrologic conditions	Attenuation Process Enhancement Evaluation
Conceptual Model – Identify contributing processes and the active zones within a plume.	●	○	● [2]	● [2]	● [2]
Conceptual Model plus Analytical Model or Mass Balance Calculation	○	●	○	○	○
Conceptual Model, possible Analytical Model, and Numerical Model	● [1]	○	●	●	●

NOTES:

¹ Numerical modelling is not necessarily preferred because costs may not be justifiable for the offsetting benefits in terms of uncertainty reduction, monitoring optimization, etc. However, numerical models may be selected if it is necessary to provide better estimates of time frames and better assurance of meeting certain types of remediation goals (e.g., concentration targets) than can be obtained with analytical modelling.

² Conceptual models are good to use for planning and site management, but may not be suited as primary support for decision making at complex sites or sites that have high uncertainty because conceptual models do not allow testing of uncertainty and parameter sensitivity and do not strongly support a detailed evaluation of enhancements.

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RT3D numerical modelling is needed when site conditions cannot be described under the simplified flow, reaction, or adsorption process assumptions that are required for use of analytical models. The groundwater flow system at a site may not be uniform because of a complex distribution of hydraulic conductivity, complex recharge/discharge elements, or transient flow conditions. Sources distributed in multiple locations, multiple contaminant species with multiple reaction pathways, and multiple oxidation/reduction conditions within the plume area cause complexities in modelling the reaction processes at a site. In some cases, assumption of linear equilibrium sorption is not appropriate, depending on the nature of the contaminant and the aquifer solids. For site conditions that include any or all of these complexities, RT3D is a more appropriate tool for modelling than use of analytical models.

Similar to analytical models, RT3D has some limitations in how it can be configured to match site conditions. A discrete numerical model cannot describe all of the nuances for each term within the transport equation. That is, RT3D cannot exactly reproduce reality because of

limitations in representing effects of the reactive transport processes at multiple scales and/or because our understanding of the processes is limited. However, compared to analytical models, RT3D can be configured to more closely match the site conditions and processes. In addition, there are also limitations in the type and quality/quantity of data that are available at any site to develop the parameters/coefficients required for the equations solved by RT3D.

A numerical model (e.g., using RT3D) can provide information to help analyze the relative importance of different fate and transport processes at an individual site and assess the plume in terms of a mass balance approach. The model can also be used to estimate the future fate and transport of contaminants. These predictions can be valuable input, along with other site information, in making timely decisions regarding implementation of remedial actions or for planning monitoring activities. A key function of the predictive capability of models is to estimate whether the remedy will meet the remediation goals when this determination cannot be made directly with field data. Numerical models, in particular, have the computational ability to estimate the interaction of multiple processes temporally and spatially for scenarios that would be difficult to assess with analytical methods.

4.0 Role of Modelling for MNA

The analysis and predictive functions of modelling are important within the context of applying MNA to 1) help analyze the relative importance of different attenuation and transport processes within a plume, 2) provide timely decision support, for instance, when there is insufficient temporal monitoring data available, 3) evaluate MNA as a remedy to replace existing remedies (e.g., P&T) that have perturbed the plume such that data to establish whether the plume is stable will not be available for a long time, 4) evaluate combinations of other remedial actions (e.g., Enhanced Attenuation) and MNA, and 5) help interpret monitoring data for transient plumes.

There are two basic capabilities of RT3D that can be applied for multiple purposes in applying MNA. The first capability is to estimate the interaction of multiple processes for fate and transport of contaminants. RT3D can also estimate the future fate and transport of contaminants and, in particular, estimate whether the MNA or MNA/EA remedy will meet remediation goals. The following sections describe these capabilities within specific roles of MNA modelling.

4.1 Attenuation Process Evaluation

RT3D can be used to assess the relative importance of attenuation processes under the specific conditions of a site. The natural attenuation capacity of the aquifer is defined as the sum of the processes that are active within the aquifer being evaluated. The rate of these processes is a function of contaminant concentration and other parameters that can vary spatially and, in some cases, temporally. Modelling analysis of these processes can provide a quantitative basis for refining the conceptual model of the site.

As a simplification, the capacity of each process to attenuate contamination can be calculated using averaged conditions for the site or for distinct portions of the site. However, to assess how these attenuation processes impact fate and transport of the contamination, the processes must be coupled and solved within a transport equation.

4.2 Timely Decision Support

If sufficient field data are not available to determine directly whether MNA will meet remediation goals, modelling, with appropriate input to describe the attenuation processes at the site, can be used to estimate whether the goals can be met. The modelling estimate and other relevant attenuation evidence provide the basis for a decision on whether to implement MNA. Continued monitoring can then be applied to verify whether the plume is behaving as expected and that remediation goals are met over time.

Example: Site “A” received waste petrochemical liquids from 1962 through 1973 in an open pit. The waste pit leaked dense non-aqueous-phase liquid (DNAPL) into a thin, moderately permeable, silt/sand unit in the subsurface where the groundwater is relatively stagnant. DNAPL contamination at the site is confined to this unit. However, the groundwater of this unit slowly

flows into a deeper sandy paleo-channel through several hydraulic conduits in the intervening clay that separates the upper silt/sand unit from the paleo-channel. Over the forty years since the waste was initially disposed of, a dissolved-phase plume of the more soluble chlorinated ethene and chlorinated ethane compounds in the waste has developed in this channel. Characterization data were collected for the plume over a period of about 5 years. The U.S. EPA MNA Protocol [U.S. EPA, 1998] was applied at the site and it was determined that there are significant attenuation processes active. However, it was not clear from the data whether the plume was stable or shrinking.

A numerical model was used to evaluate migration of the plume toward the identified receptors. Based on the modelling results and the evidence that there are significant attenuation processes at the site, MNA was approved as the remedy for the site. Monitoring is being conducted to ensure that remediation goals are met and to verify that the attenuation processes are effectively limiting plume migration. While there was not direct field evidence that the plume was currently stable or shrinking at this site, the regulatory agencies were able to support an MNA remedy based on the model predictions, the lack of risk to receptors in the near future, and the ability to effectively use monitoring to verify the MNA remedy in the near future as more data is collected to establish the trends needed to evaluate stability of the plume.

4.3 Transition to MNA from Other Remedies

For sites where another remedy is in place, the transition to MNA may require assessment of a transient plume with respect to whether MNA will be able to meet remediation goals over time. For instance, if Pump-and-Treat (P&T) is being applied to all or a portion of a plume, there will not be direct field evidence available to support a decision to transition to MNA. However, along with data to quantify the attenuation capacity, numerical modelling can be applied to predict how the plume will respond if P&T is shut down. Continued monitoring can then be used to verify whether the plume is behaving as expected and that remediation goals are met over time.

Example: Site “B” received waste petrochemical liquids from 1969 through 1980 in open pits. DNAPL migrated from the waste pits into the subsurface below the water table within alluvial deposits. Free-phase DNAPL was discovered in the subsurface during site characterization. Because the free-phase DNAPL still had the potential to migrate as a non-aqueous phase, recovery wells were installed and DNAPL extraction was initiated. In addition to direct DNAPL extraction, the DNAPL source area was surrounded by groundwater extraction wells designed to contain the dissolved-phase plume emanating from the source area and to depress the water table, in theory, to help limit vertical migration of the DNAPL. After about 5 years of operation, it was determined that the groundwater extraction was not needed to limit vertical migration of the DNAPL. The site then desired to evaluate natural attenuation as a means to limit migration of the dissolved-phase plume to protect the downgradient receptors so that groundwater extraction could be terminated.

The U.S. EPA MNA Protocol [U.S. EPA, 1998] was applied at the site and it was determined that there are significant attenuation processes active. A numerical model was used to estimate how the plume would migrate after the extraction wells were shut down. The modelling results indicated that the plume is expected to become stable within about 20 years, remain within the site property line, and not impact any receptors. The EPA approved MNA as the remedy for the dissolved-phase plume at the site and the groundwater extraction wells were shut down. Monitoring is being conducted to ensure that remediation goals are met and to verify that the attenuation processes are effectively limiting plume migration.

4.4 Evaluating Combinations of MNA and EA or Other Remedies

In some cases, MNA alone may not be able to meet remediation goals. EA may be a candidate to use in conjunction with MNA to meet these goals. However, to determine how to combine these remedies requires selecting the appropriate EA, determining performance goals for the EA, and assessing how the conditions created by the EA action will impact the natural attenuation processes. Numerical modelling can aid in this process by evaluating different scenarios for applying combined MNA/EA remedies.

For instance, if a plume is growing and it is not expected that natural attenuation processes can stabilize the plume before receptors are impacted, MNA can still be a component of the remediation strategy for the plume by 1) coupling MNA with another technology that can augment the natural attenuation capacity of the plume or 2) removing enough contaminant mass such that the natural attenuation capacity of the aquifer is sufficient to stabilize the plume. The role of numerical modelling in this case would be to aid in evaluating different combinations of technologies with MNA.

4.5 Interpreting Monitoring Data

Interpretation of monitoring data for MNA includes assessing whether natural attenuation processes are continuing to occur as expected. For plumes that are not at steady state but for which MNA was selected because the plume was predicted to reach steady state before impacting receptors, assessing the natural attenuation processes can be conducted, in part, by comparing the actual temporal changes in the plume to the model-predicted temporal changes in the plume.

Example: Site “B” (Section 4.3) had used P&T for containment of the dissolved-phase chlorinated solvent plume. Based on predictive modelling and knowledge of existing attenuation processes, the EPA approved MNA as the remedy for the dissolved-phase plume at the site and the extraction wells were shut down.

Monitoring is being conducted to ensure that remediation goals are met and to verify that the attenuation processes are effectively limiting plume migration. The model results include

concentration profiles as a function of time for each contaminant species in the dissolved-phase contaminant plume. Because the source area was hydraulically contained for about 6 years, contaminant concentrations downgradient of the source area were expected to increase after the groundwater extraction was stopped over a period of about 20 years before stabilizing. However, the concentrations are expected to increase at a rate that is much lower than would be observed if no natural attenuation occurred.

Contaminant concentration profiles are expected to follow a specific pattern based on the degradation processes observed in site-specific microcosm tests. If the actual contaminant plume is to become stable, the concentration profiles of each contaminant species should be similar to the profiles predicted by the model. Thus, the monitoring plan uses a comparison of predicted concentration profiles to measured concentration profiles to evaluate the performance of the selected MNA remedy. In the plan, three simulated concentration time profiles along a transect of the plume were developed using the model. One time profile is based on the model prediction using the natural attenuation rates that best matched the site data (baseline). Another time profile is based on a model prediction using biological natural attenuation rates that are 10% of the baseline rates. The third time profile is based on model predictions with biological natural attenuation rates set to zero. Because the concentration profile of contaminants downgradient of the source depend significantly on the magnitude of the biological natural attenuation processes, comparison of measured and predicted concentrations along a transect is considered to be an acceptable verification of whether these processes are occurring as expected. The monitoring plan outlines how the field data collected over time at this transect will be compared to these three simulated profiles. If the field data is most similar to the baseline natural attenuation simulated profile, monitoring is continued. If the field data is most similar to either of the other two simulated profiles, the MNA remedy must be re-evaluated and, potentially, contingency actions may need to be implemented.

5.0 Representation of Reactive Transport by RT3D

This section outlines how RT3D is configured for modelling reactive transport. The configuration of a numerical model must be tailored to the specific site based on the conceptual model, site hydraulic and reaction/geochemical data, and remediation goals.

RT3D provides a solution technique for the contaminant transport equation. Configuration of the model consists of determining the appropriate equation terms and setting the spatial and temporal context for solving the relevant equations. The governing equation for three-dimensional, multi-species transport in saturated porous media for constant porosity is shown in Equation 1 (adapted from Zheng and Wang [1999]). This equation shows the combination of all of the attenuation processes that contribute to the mass balance: dispersion/diffusion, advection, external sources/sinks, adsorption, and reaction. Equation 1 is a generalized form and it may be necessary to add terms (i.e., as terms of the reaction component) to describe other processes (e.g., the dissolution rate of non-aqueous phase liquid, contaminant exchange with the vadose zone, plant uptake) at a specific site.

$$\begin{array}{l}
 \text{rate of} \\
 \text{change + adsorption}
 \end{array}
 =
 \begin{array}{l}
 \text{dispersion} \\
 - \text{advection} \\
 + \text{sources} \\
 + \text{/ sinks} \\
 + \text{reaction}
 \end{array}$$

$$\frac{\partial C_k}{\partial t} + \frac{\rho_b}{\theta} \frac{\partial \hat{C}_k}{\partial t} = \frac{\partial}{\partial x_i} \left(D_{ij} \frac{\partial C_k}{\partial x_j} \right) - \frac{\partial (v_i C_k)}{\partial x_i} + \frac{q_s}{\theta} C_{s,k} + \frac{1}{\theta} \sum r_k \quad (1)$$

In Equation 1, C_k is the concentration of the k^{th} species (M/L^3), t is time (T), D_{ij} is the hydrodynamic dispersion coefficient tensor (L^2/T), x_i is the distance along the respective axis of the coordinate system (L), v_i is the linear pore water velocity (L/T), q_s is the volumetric flow rate of sources (positive) or sinks (negative) per unit volume of aquifer (L^3/T), $C_{s,k}$ is the concentration of the k^{th} species in the sources or sinks (M/L^3), θ is the porosity of the aquifer (L^3/L^3), ρ_b is the dry bulk density of the subsurface sediments (M/L^3), \hat{C}_k is the concentration of the k^{th} species on the solid phase (M/M), and r_k represents the reaction terms for transformation of the k^{th} species ($M/L^3/T$). Units are specified generically as M = mass, L = length, and T = time. Note that the linear pore water velocity times the porosity is equal to the specific discharge (Darcy flux). The reaction term r_k may be comprised of multiple terms to account for the specific reactions occurring.

RT3D obtains groundwater flow velocities from a separate flow model, typically the MODFLOW code [Harbaugh et al., 2000] with the LMT package [Zheng et al., 2001] active. Saturated groundwater flow velocities are calculated from the hydraulic-head values that are computed by MODFLOW. The flow equations used are [Zheng and Wang, 1999]:

$$v_i = -\frac{K_i}{\theta} \frac{\partial h}{\partial x_i} \quad (2)$$

$$S_s \frac{\partial h}{\partial t} = \frac{\partial}{\partial x_i} \left(K_i \frac{\partial h}{\partial x_i} \right) + q_s \quad (3)$$

In addition to previously defined variables, K_i is the principal component of the hydraulic conductivity tensor (L/T), h is the hydraulic head (L), and S_s is the specific storage coefficient (1/L) in equations 2 and 3.

To provide meaningful results, initial and boundary conditions must be established for a model based on actual physical site conditions. Initial conditions are the starting values of species concentrations (or hydraulic head for MODFLOW). Types of transport boundary conditions include defined concentrations for model boundary cells, distributed sources (e.g., recharge), and/or point sources (e.g., wells, rivers, drains, etc.).

There are specific calculation- and discretization-related errors that are inherent to solving the transport equation with numerical models. Within a numerical solution, there are tolerances for solutions, stability constraints, mass balance issues, and time-step constraints that need to be considered the numerical model setup. Numerical dispersion for solute transport, the artificial spreading of solutes to adjacent grid cells, can also be problematic for some solution techniques under conditions where the ratio of advection-related transport to dispersion-related transport is large. The MT3DMS manual [Zheng and Wang, 1999] provides a good discussion of the issues involved with artificial oscillation and numerical dispersion resulting from the advection solution procedure and model setup. Users should follow the MT3DMS guidance for appropriate values of the Peclet number, the Courant number, and maximum grid cell size changes for non-uniform grids. In addition, the user should assess the impacts of choice of advection solver, and refinements in the resolution of both the grid spacing and the transport time step size on the solution to ensure that the model setup is satisfactory. Increased resolution is not warranted at the point where there is negligible change in the results. The potential for numerical-solution related errors should be discussed when documenting a model and considered when interpreting the results.

The RT3D numerical code solves the reactive transport system described by Equation 1 using an operator-split strategy [Clement et al., 1998; Simpson et al., 2005] to uncouple the reaction terms from the advection, dispersion, and source/sink terms of the governing transport equations. These uncoupled components of the transport equation are treated as separate “packages” by RT3D in terms of the input files and the solution. In particular, the reaction terms (r_k) in Equation 1 for all contaminant species can be assembled as a set of ordinary differential equations (ODEs) that describes the reaction rate and pathway details. Specific reaction kinetic expressions may be assembled in a reaction “module” that plugs into the reaction package for solution during the overall process. RT3D includes a variety of reaction modules for specific purposes, including those designed for evaluation of MNA as a remedy for chlorinated solvent

contamination (Section 7.0). Additionally, the user may define a set of kinetic reaction expressions in a user-defined reaction module to account for processes not included in the standard reaction modules. The following sections examine the mathematical expressions of each component of the governing transport equation and discuss the type of information available to select parameter values for these expressions.

5.1 Advection

Groundwater flows primarily in response to pressure gradients. The basic relation of pressure gradients and groundwater flow is the Darcy equation. Equation 2 shows a formulation of the Darcy equation that provides the groundwater flow velocities used by RT3D in solving the transport equation.

Equation 2 illustrates that the distribution of hydraulic conductivity is the key aquifer parameter that determines the rate of groundwater flow for a given hydraulic head gradient. The flow path of groundwater is via the path of least resistance, thus developing an adequate representation of the hydraulic conductivity distribution is a key issue in configuring the numerical model.

Sources of hydraulic conductivity values include literature information, laboratory tests, and field tests. Literature information provides estimates for the intrinsic hydraulic conductivity for specific sediment types [e.g., Freeze and Cherry, 1979]. This type of information can be useful to estimate the hydraulic conductivity distribution from geologic borehole log information. There are numerous methods available to interpolate geologic data from borehole logs into a distribution of subsurface geologic layering within a defined domain (e.g., kriging techniques). The hydraulic conductivity of a specific model grid cell can be estimated using a weighted average of the intrinsic hydraulic conductivity for different sediment types (e.g., sand, silt, and clay) based on the percentage of different sediment types interpolated to the specific grid cell. Data for the intrinsic hydraulic conductivity of specific sediment types can also be estimated using site-specific tests. Sediment samples of specific sediment types can be tested in the laboratory using standard techniques to determine the permeability [e.g., Klute and Dirksen, 1986]. These techniques provide a vertical hydraulic conductivity estimate for the sediment sample that can be used to interpret the intrinsic horizontal hydraulic conductivity for the sediment type of the sample. Hydraulic properties can also be related to sediment physical properties such as grain size distributions. Field tests in selected sediment layers can be conducted as well. Typical field tests include slug tests and pumping tests. Procedures, interpretation, and limitations of these tests are readily available [e.g., Kruseman and de Ridder, 1990]. The pumping test, in particular, can be applied to evaluate the hydraulic conductivity over a larger area and determine a conductivity value that is a composite of the intrinsic conductivities for the layers present within the test area. This composite may be of value if it is not practical to represent all of the individual subsurface layers within the numerical model grid.

For the hydraulic conductivity in the vertical direction, the intrinsic conductivity approach described above can be used with values from literature, laboratory tests, or estimates based on horizontal conductivity values if the subsurface layering can be defined. If the subsurface can't be directly defined (e.g., for complex systems with layers too fine to resolve), an anisotropy factor can be used as a way to estimate the relative horizontal and vertical conductivity values. Typically transverse conductivity is assumed to be the same as the conductivity in the primary horizontal flow axis. Estimates for anisotropy are typically based on an assessment of the contrast of hydraulic conductivity between subsurface layers.

Other parameters are also important for calculating groundwater flow for some settings. For example with transient conditions, an estimate for the storage coefficient (confined aquifers) and specific yield (unconfined aquifers) is needed. Estimated values for these parameters can be obtained in the literature or from analysis of field tests. Additionally for advection velocity and transport calculations, an estimate for porosity is needed. Literature values for porosity are available based on sediment type. It is also possible to estimate porosity in the field using conservative tracer tests.

Advection can also be influenced by density differences induced by high concentrations of solutes in the groundwater [Russell et al., 1992; Barth et al., 2001; Wood et al., 2004; Simmons, 2005]. For typical MNA scenarios, density differences imposed by dispersed dissolved contaminant concentrations are not significant. However, density issues should be considered for sites that include high concentration source areas where density driven flow may have impacted the distribution of the downgradient plume or where there are natural interfaces between higher and lower density groundwater within the modelled area (e.g., for coastal areas [e.g., Smith and Turner, 2001; Westbrook et al., 2005]). Density-driven advection is not currently supported by RT3D. Advection in fractured systems is also not currently supported by RT3D.

5.2 Dispersion

Dispersion is comprised of molecular diffusion and velocity-related mechanical dispersion. In numerical modelling, dispersion is quantified using the dispersion coefficient and related tensor components representing the dispersion along the different directions. Dispersion is not readily measurable in the field and is generally viewed as a term that combines the effects of pore-scale processes and of spatial variation in hydraulic conductivity. Based on the scale of the plume, an initial estimate of an appropriate longitudinal dispersivity value can be obtained from tabulated data [e.g., Gelhar et al., 1992] or published correlations [e.g., Ayra, 1986; Pickens and Grisak, 1981; Neuman, 1990; Xu and Eckstein, 1995 and 1997; Perfect et al. 2002]. Dispersivity in the directions transverse and vertical to the plume axis is generally lower than that in the longitudinal direction. Less data is available on transverse and vertical dispersivity; that which is available is mostly of low reliability [Gelhar et al., 1992]. Rule-of-thumb type estimates are often used for transverse dispersivity (equal to 10% of longitudinal dispersivity) and vertical

dispersivity (equal to 1% of longitudinal dispersivity). The use of tabulated data and correlations based on such data has several drawbacks. First, site-specific heterogeneity is a major influence on the dispersivity, and the tabulated data is likely not specific to the site of interest. Secondly, an examination of the tabulated data will reveal that, for a give plume scale, the dispersivity can range over an order of magnitude or more.

The character of the plume concentration profiles can also provide qualitative information to assess appropriate dispersion values. For instance, plumes with sharper concentration fronts would tend to indicate lower dispersion coefficient values.

Regardless of the source of estimates, the dispersion coefficient values need to be examined as part of the calibration process. Note that the apparent dispersion may not be entirely from dispersion processes, most notably in cases where there are transient flow effects. Neglecting transience can lead to the use of “apparent transverse dispersivities” that are larger than the actual transverse dispersivity [Johnson and Spencer, 2003].

5.3 Adsorption

The most common assumption for groundwater modelling is that sorption is solely comprised of equilibrium adsorption processes (i.e., the sorption/desorption occurs much faster than the transport time scale). The most common equilibrium adsorption assumption is a linear partitioning isotherm, for which a single coefficient can be used to describe the sorption processes. This linear equilibrium partitioning coefficient, K_d (L^3/M), is defined as the ratio of the concentration of the species in the aqueous phase to the concentration of the species in the sorbed phase (Equation 4).

$$\hat{C}_k = K_{d,k} \cdot C_k \quad (4)$$

Applying the chain rule of calculus, the second term on the left hand side of Equation 1 can be expanded to

$$\frac{\partial \hat{C}_k}{\partial t} = \frac{d\hat{C}_k}{dC_k} \frac{\partial C_k}{\partial t} \quad (5)$$

If we define a retardation factor, R_k (dimensionless), for the k^{th} species as shown in Equation 6, then take the derivative of Equation 4, Equations 4, 5, and 1 can be combined into Equation 7.

$$R_k = 1 + \frac{\rho_b K_{d,k}}{\theta} \quad (6)$$

$$R_k \frac{\partial C_k}{\partial t} = \frac{\partial}{\partial x_i} \left(D_{ij} \frac{\partial C_k}{\partial x_j} \right) - \frac{\partial (v_i C_k)}{\partial x_i} + \frac{q_s}{\theta} C_{s,k} + \frac{1}{\theta} \sum r_k \quad (7)$$

The value of K_d for a chemical species can be estimated based on its relationship to other laboratory-measured parameters or through laboratory experiments. Within an aquifer, K_d values have a spatial distribution dependent on the distribution of the sediment properties that impact the partitioning process. In practice, the detail of this distribution is not known and sorption is quantified by a single coefficient over a large-scale.

In high-carbon soils, it has been demonstrated that the amount of nonionic organic chemicals sorbed varies from soil to soil and that such variations are primarily caused by the organic content of the soil [Jeng et al., 1992; Lyman et al., 1990; Bishop et al., 1989]. However, mineral-driven sorption becomes important as organic carbon content diminishes to below 0.1% [Kile et al., 1995]. At levels of organic carbon above 0.1%, the normalized sorption coefficient (K_{oc}) represents an important parameter that can be used to estimate the soil/water equilibrium partition coefficient (K_d) with this equation:

$$K_d = f_{oc} \cdot K_{oc} \quad (8)$$

where f_{oc} is the mass fraction of organic carbon (mass-oc/mass-soil) in the soil and K_d is the soil/water equilibrium partition coefficient [(mg/kg-soil)/(mg/L)]. It is important to note that at levels of organic carbon below approximately 0.1%, this relationship will likely underestimate K_d because it neglects mineral-driven sorption. In those cases, the real quantity of attached material will be higher than those predicted by Equation 8.

Many researchers have developed methods for estimating K_{oc} based on measurable properties such as the octanol/water partition coefficient (K_{ow}). Two common correlations are given in the following equations [Lyman et al., 1990; Bishop et al., 1989]:

$$\log(K_{oc}) = 3.64 - 0.55 \cdot \log(S) \quad (9)$$

$$\log(K_{oc}) = 4.277 - 0.557 \cdot \log(S_m) \quad (10)$$

where S is the water solubility of the organic compound (mg/L), and S_m is the molar water solubility of the organic compound ($\mu\text{mol/L}$).

Non-linear equilibrium relationships can also be described numerically in RT3D using data from laboratory experiments and a concentration-dependent mathematical description of a sorption/desorption isotherm (e.g., the Freundlich or Langmuir isotherms). These non-linear

equilibrium relationships may be more appropriate than a linear relationship in some aquifers [e.g., Pedit and Miller, 1994]. Karickhoff et al. [1979] suggest that non-linear relationships may be needed when contaminant concentrations are more than one half the aqueous-phase solubility of the compound or 10^{-5} M whichever is lower.

It is also possible to configure RT3D to account for non-equilibrium sorption processes. The built-in “Rate-Limited Sorption” RT3D reaction module provides an example of kinetically controlled adsorption for a single species (with no other chemical reaction). Using the typical chemical engineering approach taken by Haggerty and Gorelick [1994], the adsorption/desorption is described based on a concentration driving force and a mass transfer coefficient. The mobile and adsorbed fractions are treated as separate species, the latter of which does not undergo transport. Equations 11 and 12 describe the sorption kinetics for the mobile and immobile fractions, respectively.

$$\frac{dC_{mobile}}{dt} = -\alpha \left(C_{mobile} - \frac{C_{sorbed}}{\lambda} \right) \quad (11)$$

$$\frac{dC_{sorbed}}{dt} = \frac{\alpha\theta}{\rho_b} \left(C_{mobile} - \frac{C_{sorbed}}{\lambda} \right) \quad (12)$$

In Equations 11 and 12, α is a first-order mass-transfer rate coefficient ($1/T$), λ is a linear partitioning coefficient (i.e., K_d) (L^3/M), and the C_{mobile} and C_{sorbed} are the species concentrations (in M/L^3 and M/M , respectively). To use this non-equilibrium adsorption process, the equilibrium K_d values for both species must be set to zero. The value for λ is set as a separate parameter. As with the linear equilibrium partitioning approach, the mass transfer process has a spatial distribution dependent on the distribution of the sediment properties that impact the partitioning process. Laboratory experiments are the primary data sources for estimating the coefficients of the mass transfer approach. Presence of an irreversible sorption capacity for the aquifer can be implemented numerically as a contaminant sink.

A kinetically controlled desorption rate can provide an explanation for contaminant rebound or plume tailing effects that are sometimes observed. Several types of numerical formulations for the mass transfer relationship have been presented in the literature. One example is a two-component system combining equilibrium and kinetically controlled sorption [e.g., Brusseau and Rao, 1989]. Kinetically controlled sorption can also be modelled using a Fick’s Law approach with various assumptions related to the type of diffusional regime [e.g., Farrell et al., 1999; Farrell and Reinhard, 1994; Rugner et al., 1999; Carroll et al., 1994; Werth et al., 2000]. Alternatives to these basic approaches include dual-equilibrium models [e.g., Chen et al., 2001] or multiple mass transfer rate models [e.g., Culver et al., 1997].

5.4 Source/Sinks

There are several types of sources and sinks that can be relevant for reactive transport modelling. This section provides a brief description of NAPL dissolution (constant concentration, decaying concentration, kinetic dissolution), volatilization, groundwater influx/outflux, and phytoremediation effects.

5.4.1 NAPL-Water Mass Transfer

Quantification of a NAPL dissolution rate may be a key component for modelling some plumes with persistent source areas. There are three primary methods for modelling the interaction of NAPL and aqueous-phase contaminant concentrations.

Constant Concentration – In some cases it may be appropriate to use a boundary condition of a constant concentration in model grid cells corresponding to the location of the DNAPL source. The concentration of species for this cell can be estimated based on the effective solubility for the each species [Cohen and Mercer, 1993]. In many cases, field data indicate that the dissolved-phase concentration of DNAPL components is significantly lower than what would be predicted by the effective solubility. In these cases, the constant concentration value can be set equal to the field-observed value if the source is expected to remain for a long period of time relative to the time for transport of the plume toward the receptors.

Decaying Concentration – Dissolution of NAPL over time or application of source remediation may decrease the concentration of contaminants in the source area. As an approximation, a first-order decay in the concentration of the NAPL components (which may each decay at a different rate) in the source cells can be implemented.

Kinetic Dissolution – A kinetic expression for the DNAPL component dissolution rate can be included in the model if sufficient information is available to estimate the parameters. Similar to non-equilibrium adsorption, a mass transfer approach is used for kinetic NAPL dissolution. A driving force for the mass transfer is developed based on concentrations that can be calculated and tracked within the model. Equations 13 and 14 are an example of how non-equilibrium NAPL dissolution can be represented.

$$\frac{dC_{mobile}}{dt} = \gamma(C'_{NAPL} - C_{mobile}) \quad (13)$$

$$\frac{dC_{NAPL}}{dt} = -\frac{\gamma\theta}{\rho_b}(C'_{NAPL} - C_{mobile}) \quad (14)$$

In these equations, C_{mobile} is the aqueous-phase concentration of the NAPL species (M/L^3), C_{NAPL} is the mass of NAPL-phase per unit aqueous volume (M/L^3), C'_{NAPL} is the solubility of the NAPL

species, and γ is a mass transfer coefficient (1/T). Additional information about DNAPL dissolution mechanisms is available in the literature [e.g., Clement et al., 2004a and 2004b; Miller et al., 1990 and 1998; Powers et al., 1991 and 1994].

5.4.2 Volatilization

There are three mass transfer processes that must be quantified to estimate the overall transfer of chlorinated solvents from the groundwater to the gas phase in the vadose zone. Figure 1 illustrates the concept applied for mass transfer at the groundwater table interface. At this interface, there is a mass transfer resistance associated with chlorinated solvent molecules crossing the interface. On either side of this interface, there are diffusion layers (gas film and liquid film) that affect the rate at which the chlorinated solvent can reach the groundwater table interface from the bulk groundwater and the rate at which the chlorinated solvent can move away from the interface into the bulk vadose zone gas phase. The estimate of overall mass transfer rate is a function of the parameters that control these three mass transfer processes.

The parameter controlling mass transfer at the groundwater table interface is the Henry's Law equilibrium partitioning coefficient. The Henry's Law coefficient is expressed as the concentration of a species in the vapor phase divided by the concentration of the species in the aqueous phase when these two phases are in equilibrium with respect to the species of interest. Chlorinated solvents have a relatively high Henry's Law coefficient; consequently, they can readily partition into the vapor phase across the groundwater table interface.

The diffusion processes to and away from the groundwater table interface are controlled by the diffusion coefficient in the medium (water or air) and the thickness of the diffusion layer. The diffusion coefficients for chlorinated solvents are on the order of 1×10^{-6} cm²/s and 1×10^{-2} cm²/s in water and air, respectively [Lyman et al., 1990]. The thickness of the diffusion layer is dependent on the hydraulic regime and physical nature of the liquid-gas system. The diffusion

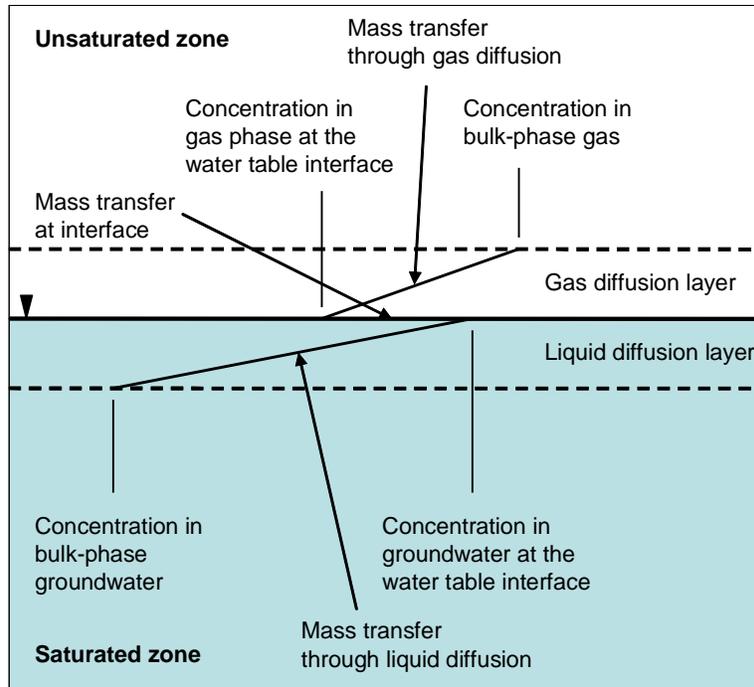


Figure 1. Mass Transfer Concept at the Groundwater Table Interface

layer thickness in the gas phase and groundwater must be estimated for the given site conditions. The mass transfer rate is significantly influenced by the diffusion layer thickness in the groundwater and minimally influenced by the diffusion layer thickness in the gas phase.

Using the above mechanisms, the mass transfer rate at the groundwater table as a function of bulk groundwater concentration can be estimated. Being a single (aqueous) phase code, RT3D does not have a built in method for describing volatilization. However, the mass transfer due to volatilization could be represented in a user-defined reaction module where model grid cells at the water table have an additional loss term. The volatilization loss term could use a lumped mass transfer coefficient similar to the approach for non-equilibrium NAPL dissolution or could use a resistance-in-series approach with individual mass transfer coefficients for the zones described above.

5.4.3 Groundwater Influx/Outflux

Introduction or removal of contaminants from the groundwater system can be an important factor in assessing the mass balance of the contaminant plume, depending on the specific site. Natural (e.g., recharge, evapotranspiration, rivers, drains) and introduced (extraction and injection wells) can be specified in MODFLOW/RT3D as sources/sinks for groundwater flow and thus for contaminant mass carried with the groundwater. Extraction and injection wells may be important as part of modelling, for instance, EA/MNA combinations.

5.4.4 Phytoremediation Effects

There are three primary functions of phytoremediation that may need to be incorporated into modelling analysis. First, in some phytoremediation applications, plants can uptake and remove a significant amount of groundwater from the aquifer. This hydraulic impact on the aquifer can be applied as a water sink (e.g., a well) within the modelled domain or through evapotranspiration. Information about the rate of removal or the resultant cone of depression around the plants is needed to establish the parameters for this water sink. Second, phytoremediation may directly remove contaminant from the aquifer (e.g., through uptake and subsequent transpiration or in-plant degradation of the contamination). This contaminant impact can be incorporated with the hydraulic impact as part of the water sink. Lastly, phytoremediation may enhance or change existing degradation processes within a defined portion of the aquifer. These impacts on degradation processes may be the result of synergistic effects between the plant roots and the microbial population or perhaps caused by changing redox conditions. These degradation processes can be implemented in the same way that other spatial variations in reaction processes are included in the model configuration (Section 5.5 below). Information about the specific reactions and rates that occur in the phytoremediation zone are needed to select the appropriate rate expressions and coefficients for the model.

5.5 Biological and Chemical Reactions

The final term of the governing transport equation is the reaction component. The RT3D reaction module is used to encapsulate the factors that comprise the reaction term of the governing transport equation, including non-equilibrium mass transfer (e.g., adsorption, NAPL dissolution) and biological and chemical reactions. This section discusses the basis for modelling biological dechlorination reactions, while Section 6.0 describes the biological and abiotic dechlorination reactions that may occur for chlorinated ethenes, ethanes, and methanes.

Biological and chemical reaction processes can be described mechanistically or with general empirical relationships. For numerical groundwater modelling, empirical relationships providing an estimate of the overall rate of transformation and dependence of this rate on the concentrations of chemical species related to the transformation reaction are typically used. Contaminant transformation processes under natural attenuation conditions are typically described using a lumped first-order kinetic form (e.g., Equation 15) that has been effective in simulating transformation rates under a variety of conditions [U.S. EPA, 1998; Clement et al., 2000] (but see Johnson and Truex [2006] for discussion on the suitability of first-order expressions). It is also feasible to add dependencies of this rate related to the concentration of reactants or inhibitors. Common forms for reaction dependencies, such as for oxidation/reduction state or specific reactant concentration, include inhibition terms and Monod-type terms as shown by Equations 16 and 17, respectively.

$$\frac{dC_k}{dt} = -k_{fwd} \cdot C_k \quad (15)$$

$$\frac{dC_k}{dt} = \left(\frac{-k_{fwd} \cdot C_k}{K_C \cdot \left(1 + \frac{C_{inhibitor}}{K_i} \right) + C_k} \right) \quad (16)$$

$$\frac{dC_k}{dt} = \left(\frac{-k_{fwd} \cdot C_k}{K_C + C_k} \right) \quad (17)$$

In Equations 16 and 17, k_{fwd} is the first-order rate coefficient for the k^{th} species (1/T), K_C is the half saturation coefficient (M/L³), $C_{inhibitor}$ is the concentration of an inhibitor species (M/L³), and K_i is an inhibition coefficient (M/L³).

While there are other factors that can impact dechlorination activity of bacteria, dechlorination reaction pathways and rates have been shown to vary as a function of the electron acceptor conditions. Hence, the electron acceptors and other geochemical indicators (e.g., redox potential, methane, total organic carbon, etc.) usually categorize the overall activity of bacteria at the site. In general, the sequence of electron acceptors (non-contaminant) from more oxidizing to more reducing conditions are: oxygen, nitrate, iron/manganese, sulfate, and carbon dioxide (methane production).

Section 6.0 discusses the dechlorination reactions as a function of three basic geochemical settings at a site: Aerobic, Anoxic, and Anaerobic. In most cases, the geochemical data available at a site is sufficient to identify which of these three settings describes the site or to divide the site into several segments with different geochemical settings (e.g., an anaerobic portion near the source and an aerobic portion at some point downgradient of the source). Using this type of information, RT3D can be configured to model these different redox zones reactions and rates specific to the geochemical setting in each zone [e.g., Johnson et al., 2003]. Alternatively, if a significant amount of temporal and spatial data are available/collected at a site, the oxidation/reduction conditions at any given point in the model can be explicitly modelled and RT3D can use this information to model the dechlorination reactions as a function of these conditions within each model grid cell. These two approaches are discussed further in Section 8.2.2.

In some cases, it may be useful to describe both the substrate and the electron acceptor reactions and the correlation of these reactions to dechlorination rates. Expressions for these reactions can be developed based on knowledge of the metabolic respiration processes that have been

examined in the literature or laboratory. This approach requires an in-depth knowledge of the metabolic processes at a site and adds additional parameters for which estimates are required. However, the basic approach of describing the correlation between substrate and electron acceptor reactions and dechlorination rate can be constructed and implemented with appropriate assumptions about the dependency of the dechlorination rate on the concentration of other species (e.g., electron acceptors) in the groundwater, thus simplifying the expressions. A key limitation of this approach for natural attenuation modelling is that the substrate type and flux is not well defined under natural attenuation conditions. Thus, assumptions about the metabolic reactions are typically necessary. More typically, kinetic expressions incorporating substrate and electron acceptor reactions and the correlation of these reactions to dechlorination rates are applied for accelerated bioremediation applications where there is much better information about the type and flux of the substrate.

Sources of information on reaction processes and rate coefficients relevant to numerical modelling include laboratory studies, literature information, and in some cases, field data. Laboratory microcosm tests provide data on the type of reactions and rate of reactions that occur in a sediment sample under the conditions of the microcosm experiment. It is not possible to duplicate the exact conditions in the field within the microcosm test. Additionally, the sediment for the test has been disturbed and taken out of its context with surrounding sediment. However, if care is taken to maintain conditions in the microcosm that are similar to the conditions in the aquifer, the data can be useful to derive a description of relevant reaction processes for the area of the aquifer represented by the sediment and conditions of the microcosm test. The reaction rates determined in the microcosm test are typically higher than the reaction rates that can be expected in the field. However, the relative rates of different reaction processes (e.g. the rate of TCE transformation relative to the rate of DCE transformation) are likely to be consistent between the laboratory and the field. It is then necessary within model calibration to estimate the correction factor between the laboratory-derived rates and the rates in the field. It has typically been the practice to determine site-specific transformation rates, but there are rate data available in the literature that may provide useful information for comparison to the site-specific rates. It may also be reasonable in some cases to use reaction process and rate data from other similar sites as a starting point for developing the reaction processes at a site. Microbial characterization of the site may be of use to establish whether specific organisms, such as those of the *dehalococcoides* genus, are present as a guide for interpreting the probable reaction processes.

6.0 Description of Dechlorination Reactions

The geochemical conditions at a site significantly impact the type of dechlorination reactions that will occur. At one end of the geochemical spectrum is the aerobic geochemical setting where oxygen is present as the primary electron acceptor for subsurface bacteria. Because oxygen is generally preferred by bacteria over all other electron acceptors and is toxic to many anaerobic bacteria, the presence of oxygen defines a very specific type of bacterial activity. Once oxygen concentration drops below about 10% of its solubility limit, the activity of aerobic bacteria and the toxic effect of oxygen are greatly diminished. When oxygen is absent and there is sufficient substrate for anaerobic bacteria to flourish, there are clear end products that serve as indicators of significant anaerobic activity. Depending on the type of anaerobic bacteria that are dominating the subsurface, methane, reduced iron, and/or sulfide will be present and the concentrations of more oxidized electron acceptors such as nitrate and sulfate will be low. Under these anaerobic conditions, it has been demonstrated that dechlorination reactions usually occur in conjunction with the anaerobic activity that produces the indicator compounds. The anoxic geochemical condition describes the type of conditions where oxygen is not present at high enough levels to inhibit the activity of other bacteria, but there are no, or limited, indicators of significant anaerobic bacterial activity. It is more difficult to determine the type of biological dechlorination reactions that are occurring at the site under anoxic conditions. However, biological dechlorination reactions may still be a significant attenuation mechanism. Typically under the anoxic geochemical setting, more detailed investigations are needed to fully quantify the rate and extent of biological dechlorination at the site.

Abiotic chemical reactions can either be water-phase reactions, or catalyzed by aquifer materials. Water-phase abiotic reactions are included as part of the reaction tables below. These reactions are usually not significantly impacted by the geochemical conditions, though the rate of reaction is a function of temperature and, in some cases, pH. Catalyzed abiotic reactions are not included as a separate category below, but are considered as part of the reactions that are dependent on sediment components such as iron. These reactions are considered to be essentially coupled with the corresponding biological reactions that reduce/oxidize aquifer sediment component

Table 2 lists the chlorinated chemical species under consideration in this document by contaminant group along with their abbreviation and chemical formula. The types of biological and abiotic dechlorination reactions that can occur are described in Table 3.

Table 2. Chlorinated Contaminant Species by Contaminant Type

Contaminant Group	Abbreviation	Chemical Formula	Contaminant Name	Synonyms
Chloroethenes	PCE	$\text{CCl}_2=\text{CCl}_2$	Tetrachloroethene	Tetrachloroethylene, Perchloroethene
	TCE	$\text{CHCl}=\text{CCl}_2$	Trichloroethene	Trichloroethylene
	1,2-cis-DCE	$\text{CHCl}=\text{CHCl}$	cis-1,2-Dichloroethene	cis-1,2-Dichloroethylene, cis-DCE, c-DCE
	1,2-trans-DCE	$\text{CHCl}=\text{CHCl}$	trans-1,2 -Dichloroethene	trans-1,2-Dichloroethylene, trans-DCE, t-DCE
	1,1-DCE	$\text{CCl}_2=\text{CH}_2$	1,1-Dichloroethene	1,1-Dichloroethylene, Vinylidene Chloride
	VC	$\text{CH}_2=\text{CHCl}$	Chloroethene	Vinyl Chloride, Chloroethylene
Chloroethanes	1,1,2,2-TeCA	$\text{CHCl}_2-\text{CHCl}_2$	1,1,2,2-Tetrachloroethane	—
	1,1,2-TCA	$\text{CH}_2\text{Cl}-\text{CHCl}_2$	1,1,2-Trichloroethane	Vinyl Trichloride
	1,2-DCA	$\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$	1,2-Dichloroethane	Ethane Dichloride
	1,1,1,2-TeCA	$\text{CHCl}-\text{CCl}_3$	1,1,1,2-Tetrachloroethane	—
	1,1,1-TCA	CH_3-CCl_3	1,1,1-Trichloroethane	—
	1,1-DCA	$\text{CH}_3-\text{CHCl}_2$	1,1-Dichloroethane	—
	CA	$\text{CH}_3-\text{CH}_2\text{Cl}$	Chloroethane	Ethyl Chloride
Chloro-methanes	CT	CCl_4	Tetrachloromethane	Carbon Tetrachloride
	CF	CHCl_3	Trichloromethane	Chloroform
	DCM	CH_2Cl_2	Dichloromethane	Methylene Dichloride, Methylene Chloride
	CM	CH_3Cl	Chloromethane	Methyl Chloride

Table 3. Descriptions of Biological and Abiotic Dechlorination Reactions

Reaction	Abbreviation	Description
Aerobic Cometabolism	ACM	Dechlorination of a compound where the compound is fortuitously degraded by an enzyme used in cellular metabolism – typically a monooxygenase enzyme.
Aerobic Direct Metabolism	ADM	Use of the chlorinated compound as an electron donor for aerobic metabolism.
Abiotic Hydrolysis	AH	Homogeneous abiotic dechlorination – no specific reaction for this classification.
Anaerobic Cometabolism	ANCM	Dechlorination of a compound where the compound is fortuitously used as a surrogate electron acceptor, though the cell does not gain energy by reduction of the compound. For the reactions listed as ANCM, denitrification is an example metabolic process that supports this activity.
Anaerobic Direct Metabolism	ANDM	Use of the chlorinated compound as an electron donor for anaerobic respiration – typically coupled to iron reduction.
Dichloroelimination (biotic)	DC	Dechlorination of a compound where the compound is used as an electron acceptor, the bacteria may or may not gain energy by reduction of the compound. This reaction removes two chloride atoms in an elimination reaction. The more general term for this reaction is dihaloelimination, but may also be referred to as vicinal reduction.
Dehydrochlorination (abiotic)	DHC	This reaction removes one chloride atom and one proton in an elimination reaction. This reaction is usually referred to as abiotic, but studies indicate that the reaction can be enhanced/catalyzed by bacteria and/or minerals (e.g., clay). The more general term for this reaction is dehydrohalogenation and is sometimes referred to as dehydrodehalogenation.
Reductive Dechlorination (biotic)	RD	Dechlorination of a compound where the compound is used as an electron acceptor, the bacteria may or may not gain energy by reduction of the compound. This reaction removes one chloride atom from the compound and replaces it with a proton. This reaction is sometimes referred to as hydrogenolysis.

Based on the characteristics of the geochemical settings, some dechlorination reactions are very likely to occur, some highly unlikely to occur, and some may occur depending on specific circumstances. Figures 2 through 13 (after Truex et al. [2006]) illustrate the dechlorination reactions that may occur at a site depending on the geochemical conditions and contaminants

present. These figures depict the reactions most likely to occur at a site and can be used to assess what other reactions are possible, but may need more detailed information to quantify. Rates, in the form of the half-life in years at a temperature of 25°C and pH of 7, are presented for water-phase abiotic reactions that always occur and are not significantly dependent on site conditions. Rates for the other biologically catalyzed reactions cannot be defined generically. Nomenclature for each reaction type is listed in Table 3. References for laboratory data describing each reaction (except those noted as “highly unlikely”) are provided corresponding to the footnote numbers shown in the figures. The references are not intended to represent an exhaustive literature review, but provide examples of laboratory information that is available to describe the reactions. For the geochemical setting categorization, the anaerobic and aerobic settings are defined such that they represent conditions where it is highly likely that specific reactions are occurring. For some reactions, additional information is also needed under aerobic or anaerobic geochemical settings to determine whether the reaction is occurring at a site. The anoxic geochemical setting represents sites where the criteria used to define the general geochemical conditions are not sufficient to determine the specific reactions that are likely to occur. Thus, for anoxic geochemical settings, more detailed information is always needed to determine what reactions are occurring. Based on the nomenclature and description in Table 3, Table 4 describes the type of additional characterization information that is necessary to determine whether a reaction is occurring.

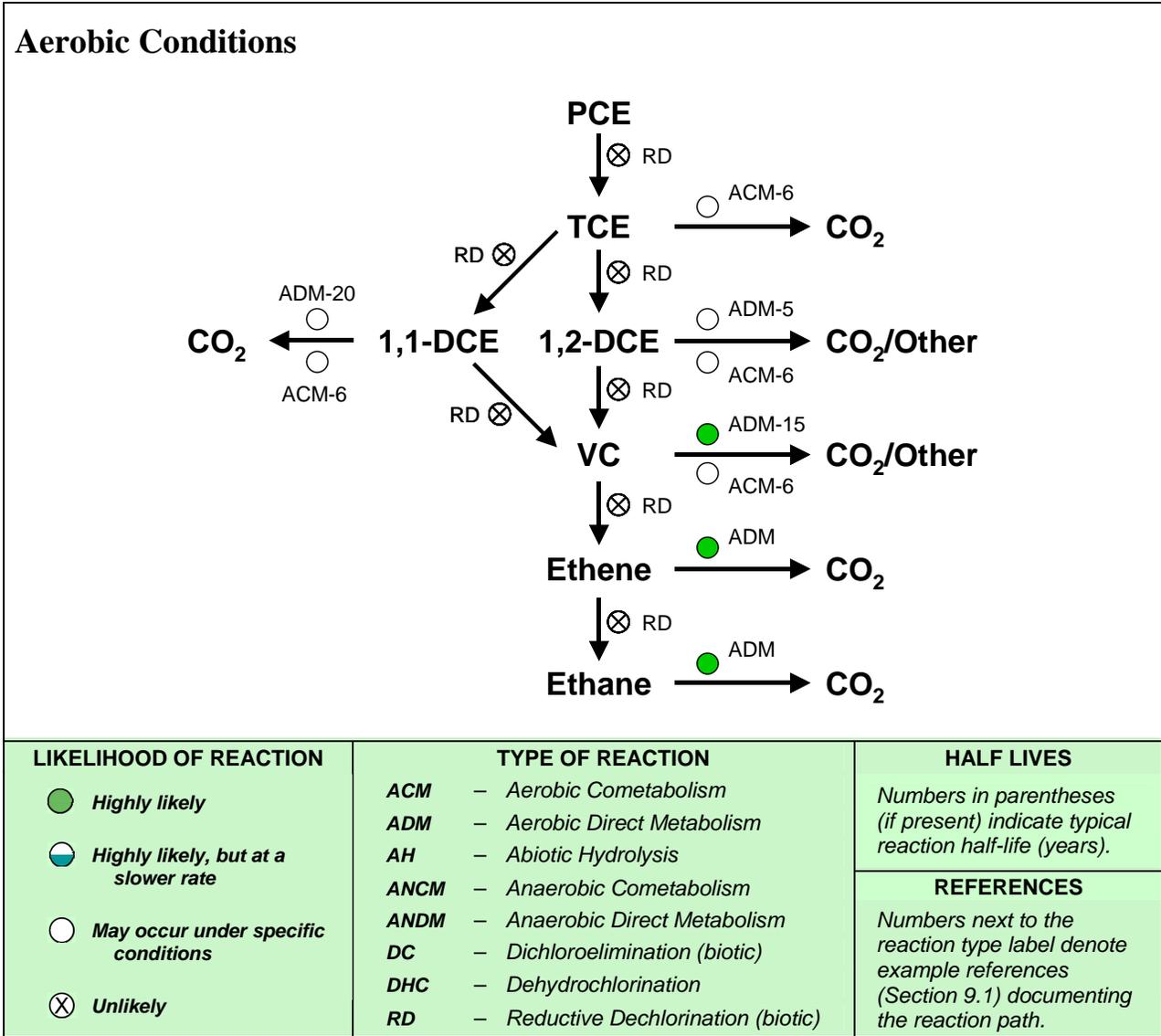
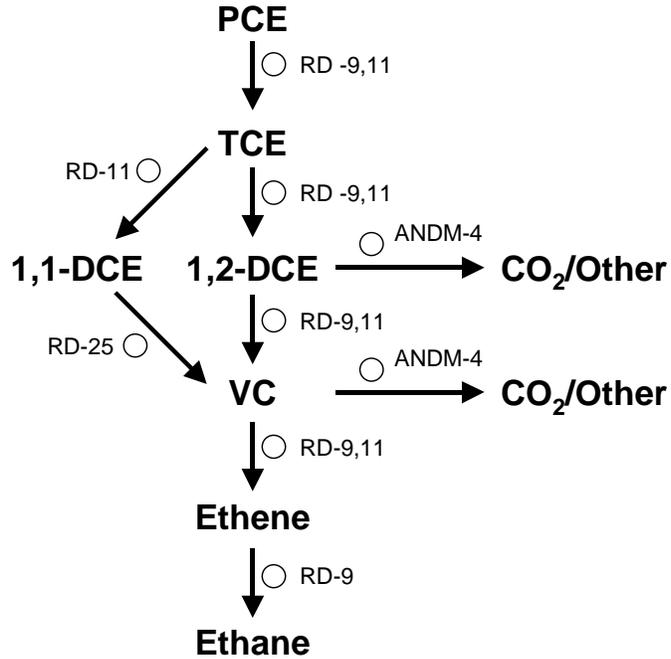


Figure 2. Dechlorination Reactions for PCE under the Aerobic Geochemical Setting

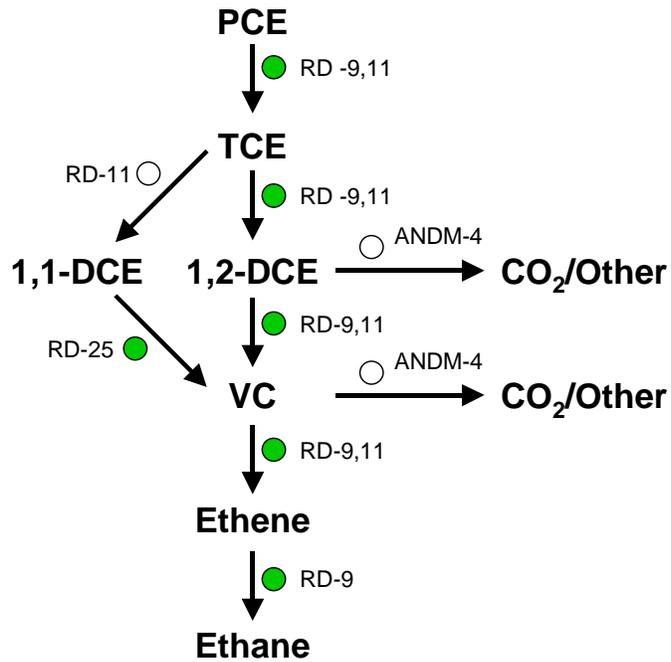
Anoxic Conditions



LIKELIHOOD OF REACTION	TYPE OF REACTION	HALF LIVES
● <i>Highly likely</i>	ACM – Aerobic Cometabolism	Numbers in parentheses (if present) indicate typical reaction half-life (years).
◐ <i>Highly likely, but at a slower rate</i>	ADM – Aerobic Direct Metabolism	
○ <i>May occur under specific conditions</i>	AH – Abiotic Hydrolysis	REFERENCES Numbers next to the reaction type label denote example references (Section 9.1) documenting the reaction path.
⊗ <i>Unlikely</i>	ANCM – Anaerobic Cometabolism	
	ANDM – Anaerobic Direct Metabolism	
	DC – Dichloroelimination (biotic)	
	DHC – Dehydrochlorination	
	RD – Reductive Dechlorination (biotic)	

Figure 3. Dechlorination Reactions for PCE under the Anoxic Geochemical Setting

Anaerobic Conditions



LIKELIHOOD OF REACTION	TYPE OF REACTION	HALF LIVES
● <i>Highly likely</i>	<i>ACM</i> – Aerobic Cometabolism	<i>Numbers in parentheses (if present) indicate typical reaction half-life (years).</i>
◐ <i>Highly likely, but at a slower rate</i>	<i>ADM</i> – Aerobic Direct Metabolism	
○ <i>May occur under specific conditions</i>	<i>AH</i> – Abiotic Hydrolysis	REFERENCES <i>Numbers next to the reaction type label denote example references (Section 9.1) documenting the reaction path.</i>
⊗ <i>Unlikely</i>	<i>ANCM</i> – Anaerobic Cometabolism	
	<i>ANDM</i> – Anaerobic Direct Metabolism	
	<i>DC</i> – Dichloroelimination (biotic)	
	<i>DHC</i> – Dehydrochlorination	
	<i>RD</i> – Reductive Dechlorination (biotic)	

Figure 4. Dechlorination Reactions for PCE under the Anaerobic Geochemical Setting

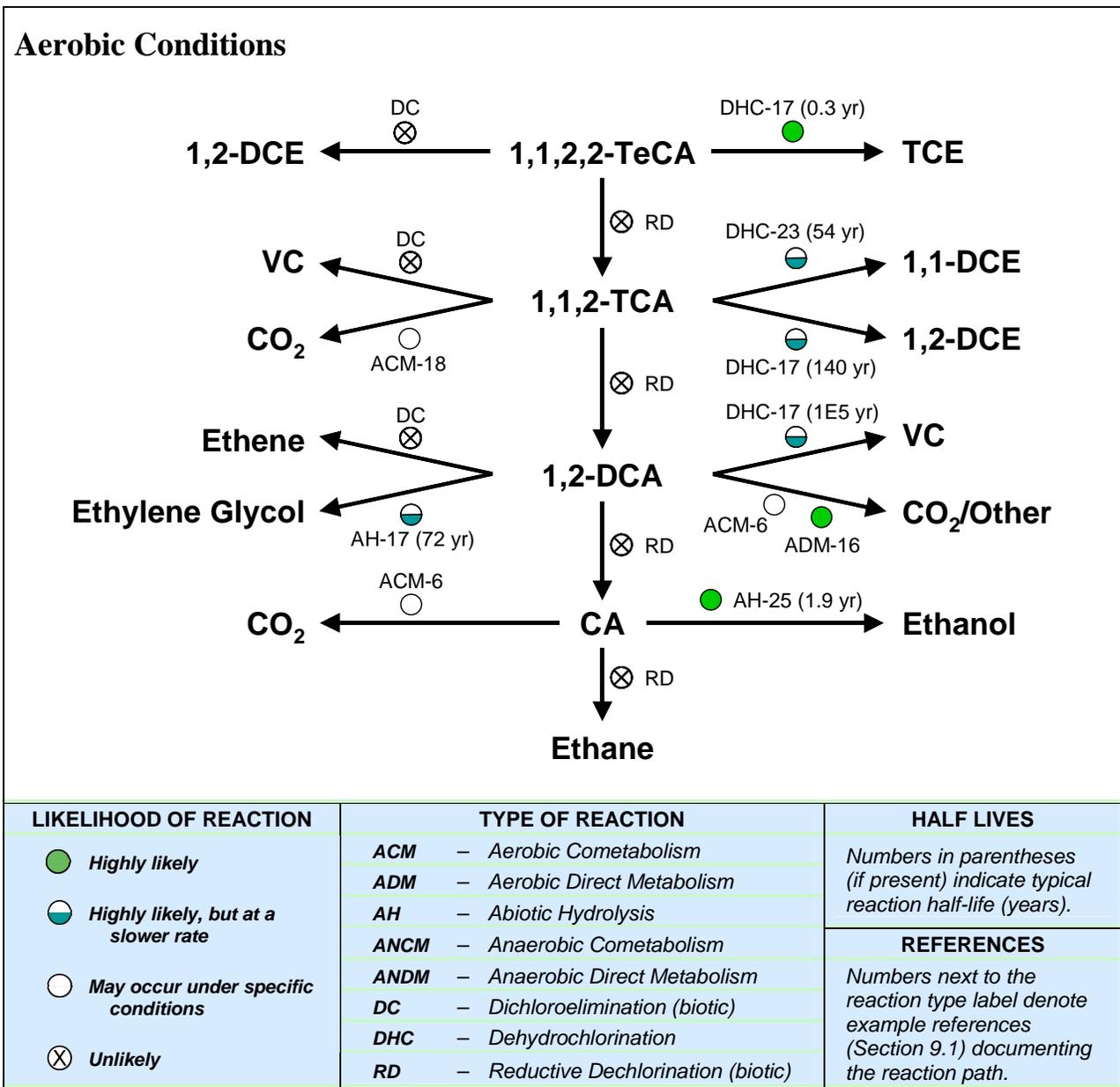


Figure 5. Dechlorination Reactions for 1,1,2,2-TeCA under the Aerobic Geochemical Setting

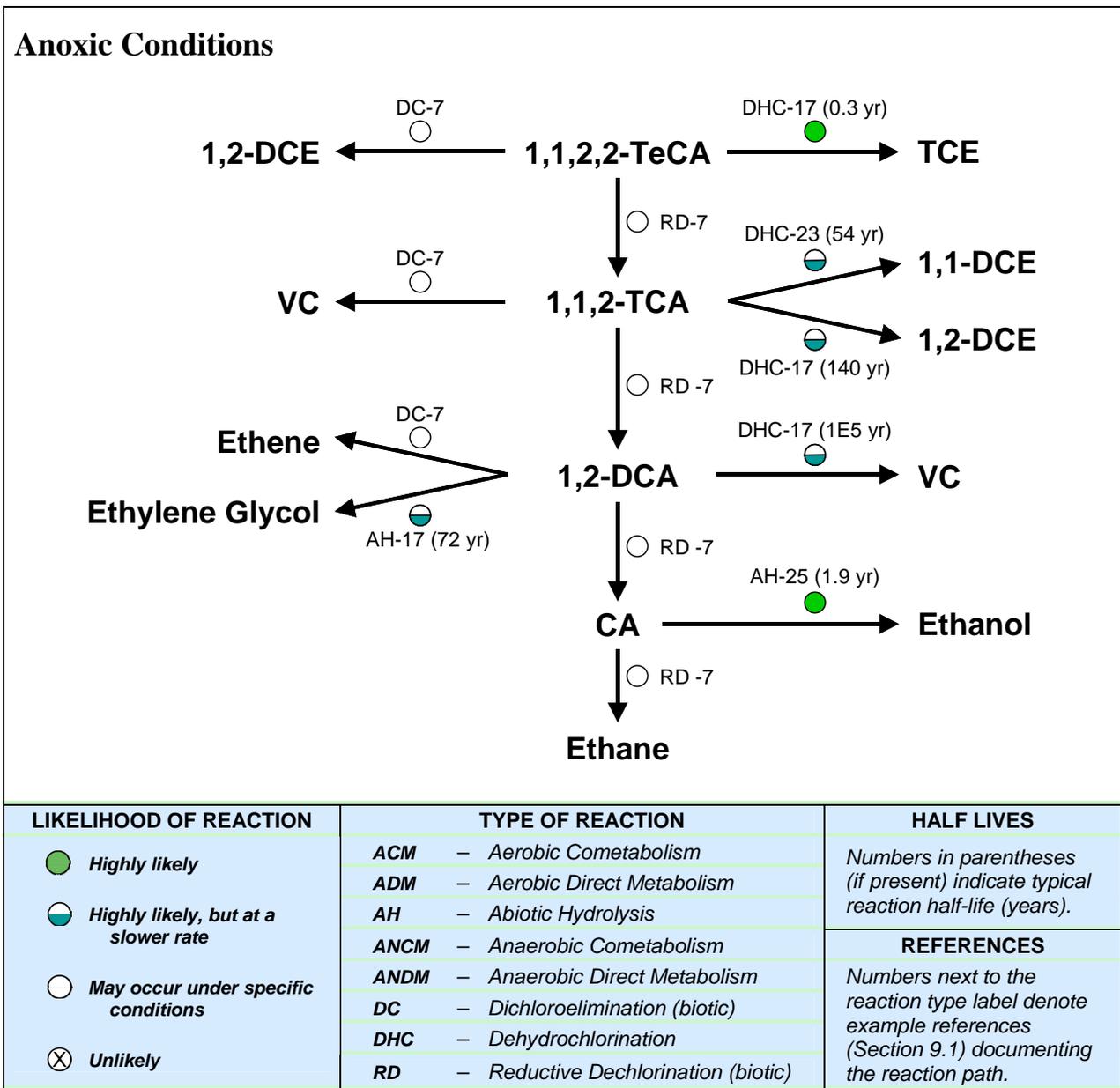


Figure 6. Dechlorination Reactions for 1,1,2,2-TeCA under the Anoxic Geochemical Setting

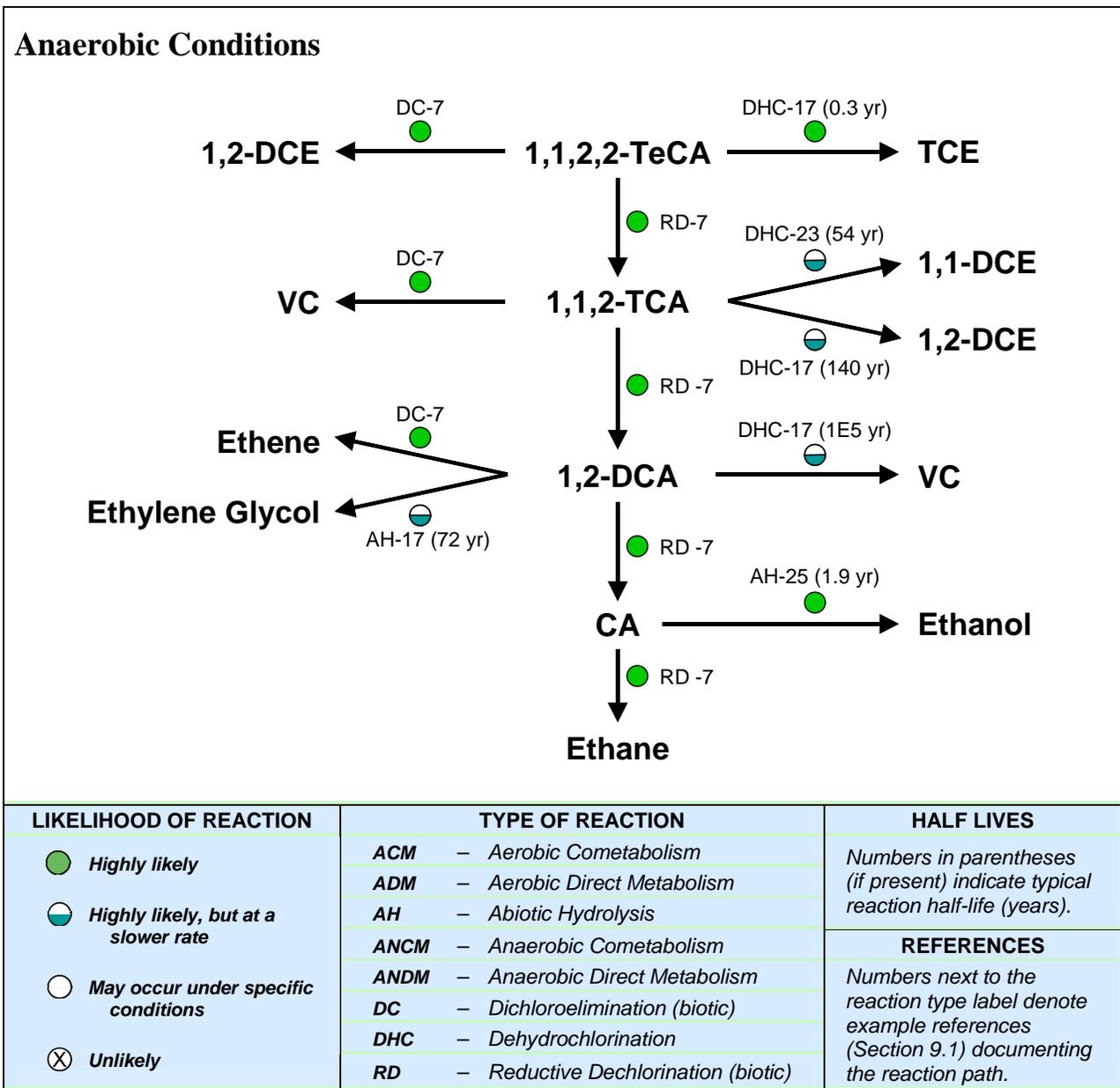
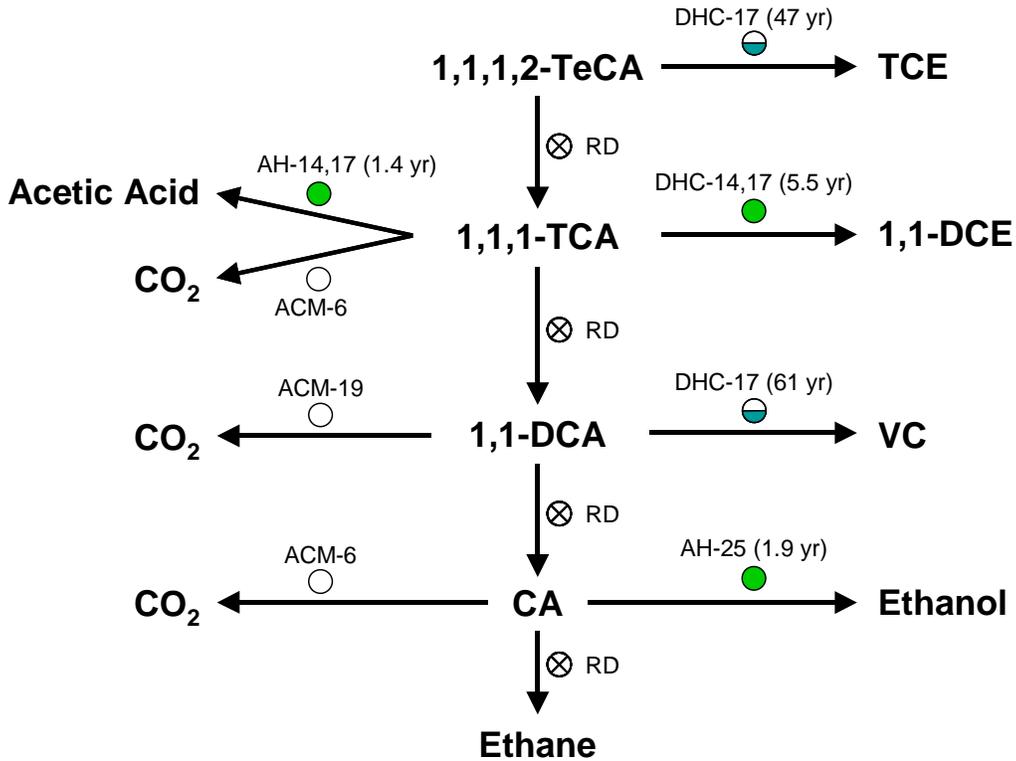


Figure 7. Dechlorination Reactions for 1,1,2,2-TeCA under the Anaerobic Geochemical Setting

Aerobic Conditions



LIKELIHOOD OF REACTION	TYPE OF REACTION	HALF LIVES
● Highly likely	ACM – Aerobic Cometabolism	Numbers in parentheses (if present) indicate typical reaction half-life (years).
◐ Highly likely, but at a slower rate	ADM – Aerobic Direct Metabolism	
○ May occur under specific conditions	AH – Abiotic Hydrolysis	REFERENCES Numbers next to the reaction type label denote example references (Section 9.1) documenting the reaction path.
⊗ Unlikely	ANCM – Anaerobic Cometabolism	
	ANDM – Anaerobic Direct Metabolism	
	DC – Dichloroelimination (biotic)	
	DHC – Dehydrochlorination	
	RD – Reductive Dechlorination (biotic)	

Figure 8. Dechlorination Reactions for 1,1,1,2-TeCA under the Aerobic Geochemical Setting

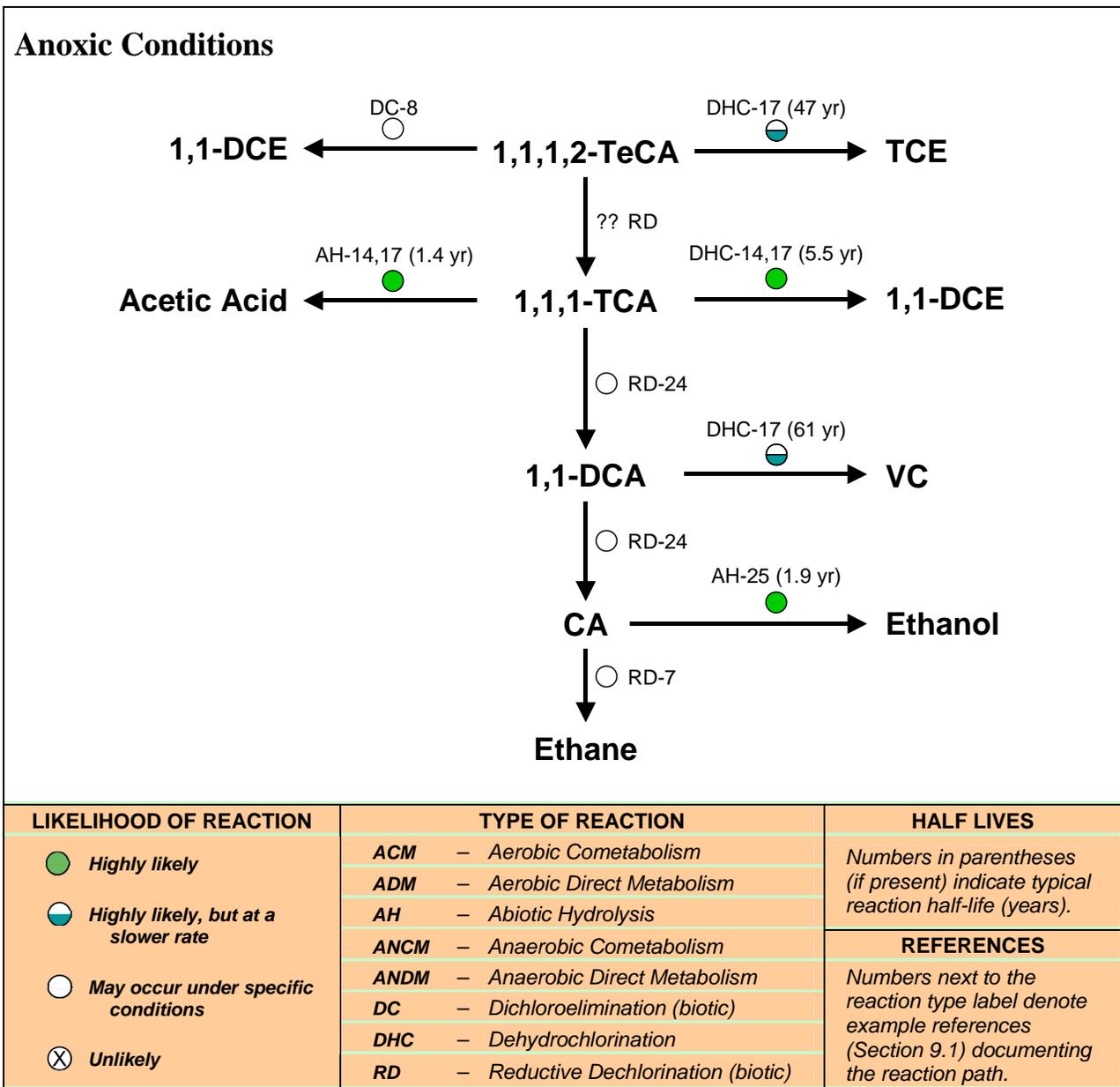


Figure 9. Dechlorination Reactions for 1,1,1,2-TeCA under the Anoxic Geochemical Setting

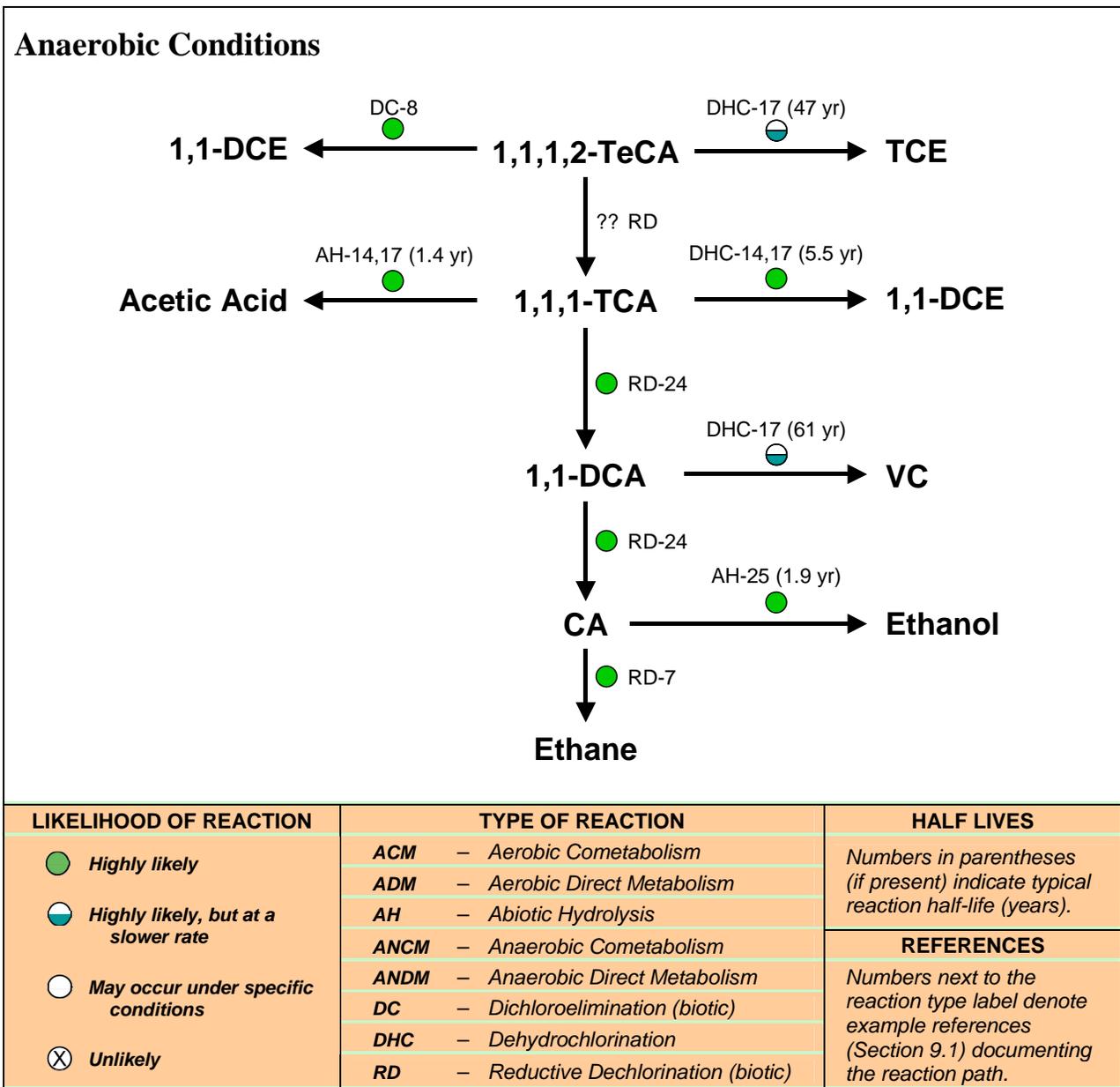


Figure 10. Dechlorination Reactions for 1,1,1,2-TeCA under the Anaerobic Geochemical Setting

Aerobic Conditions

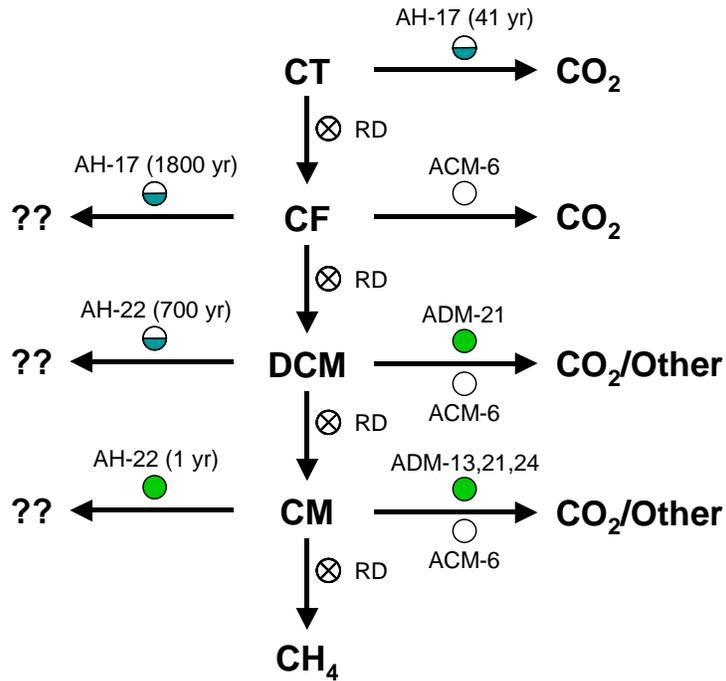
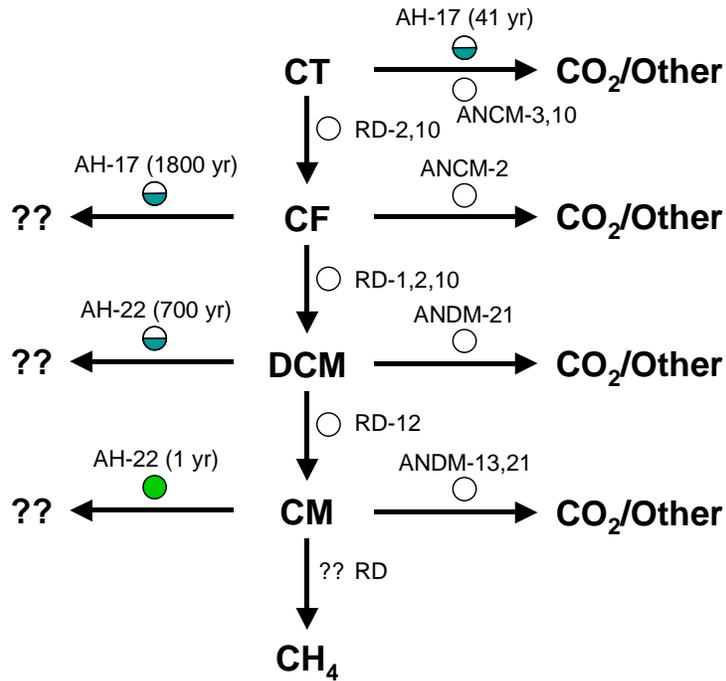


Figure 11. Dechlorination Reactions for CT under the Aerobic Geochemical Setting

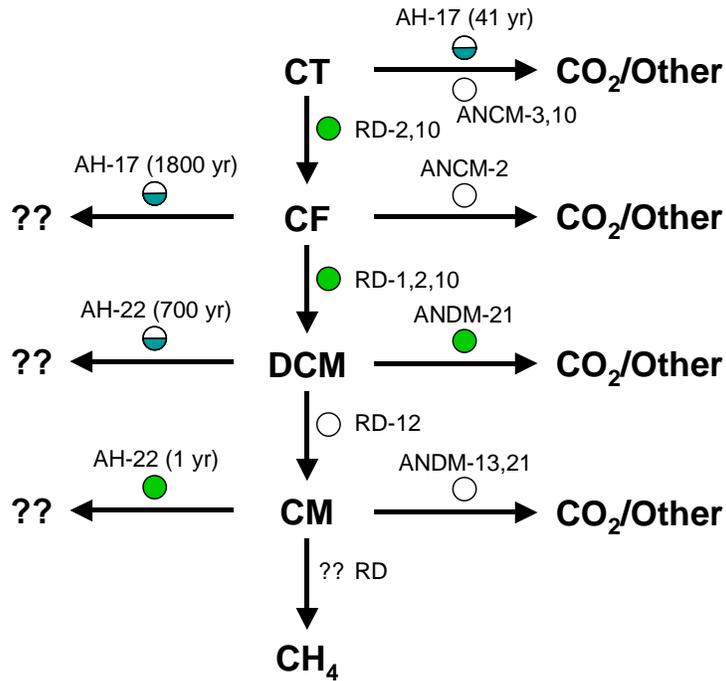
Anoxic Conditions



LIKELIHOOD OF REACTION	TYPE OF REACTION	HALF LIVES
● Highly likely	ACM – Aerobic Cometabolism	Numbers in parentheses (if present) indicate typical reaction half-life (years).
◐ Highly likely, but at a slower rate	ADM – Aerobic Direct Metabolism	
○ May occur under specific conditions	AH – Abiotic Hydrolysis	REFERENCES Numbers next to the reaction type label denote example references (Section 9.1) documenting the reaction path.
⊗ Unlikely	ANCM – Anaerobic Cometabolism	
	ANDM – Anaerobic Direct Metabolism	
	DC – Dichloroelimination (biotic)	
	DHC – Dehydrochlorination	
	RD – Reductive Dechlorination (biotic)	

Figure 12. Dechlorination Reactions for CT under the Anoxic Geochemical Setting

Anaerobic Conditions



LIKELIHOOD OF REACTION	TYPE OF REACTION	HALF LIVES
● Highly likely	ACM – Aerobic Cometabolism	Numbers in parentheses (if present) indicate typical reaction half-life (years).
◐ Highly likely, but at a slower rate	ADM – Aerobic Direct Metabolism	
○ May occur under specific conditions	AH – Abiotic Hydrolysis	REFERENCES Numbers next to the reaction type label denote example references (Section 9.1) documenting the reaction path.
⊗ Unlikely	ANCM – Anaerobic Cometabolism	
	ANDM – Anaerobic Direct Metabolism	
	DC – Dichloroelimination (biotic)	
	DHC – Dehydrochlorination	
	RD – Reductive Dechlorination (biotic)	

Figure 13. Dechlorination Reactions for CT under the Anaerobic Geochemical Setting

Table 4. Additional Characterization Information to Assess Whether a Reaction Will Occur

Reaction	Abbreviation	Characterization Information
Aerobic Cometabolism	ACM	A source of methane or other co-substrates for these reactions that is migrating into an aerated portion of the aquifer needs to be present to provide the driving force for these reactions.
Aerobic Direct Metabolism	ADM	No additional information is needed.
Abiotic Hydrolysis	AH	Confirm temperature and pH for use of half-life values in figures and to adjust as needed based on root data and equations in noted references.
Anaerobic Cometabolism	ANCM	This type of reaction typically occurs with denitrification. Thus, evidence of active denitrification and an energy source to drive this reaction (e.g., organic acids) is needed to verify that this reaction is occurring.
Anaerobic Direct Metabolism	ANDM	Anaerobic direct metabolism is typically linked to utilization of an electron acceptor such as iron. Thus, evidence of this type of reduction is needed to assess whether this reaction is occurring.
Dichloroelimination (biotic)	DC	This reaction occurs under geochemically reduced conditions. The specific daughter products produced by DC should also be present in most cases. Especially under the anoxic geochemical setting, microcosm tests with site-specific sediments may be needed to verify this reaction.
Dehydrochlorination (abiotic)	DHC	Confirm temperature and pH for use of half-life values in figures and to adjust as needed based on root data and equations in noted references. This reaction may also be enhanced under geochemically reduced conditions. Microcosm tests with site-specific sediments may be needed to verify any enhancement.
Reductive Dechlorination (biotic)	RD	This reaction occurs under geochemically reduced conditions. The specific daughter products produced by RD should also be present in most cases. Especially under the anoxic geochemical setting, microcosm tests with site-specific sediments may be needed to verify this reaction.

7.0 Selection of a Reaction Module

RT3D provides a suite of reaction modules for use in modelling MNA or MNA/EA of the chlorinated solvents listed in Table 2. Figure 14 shows the basic decision process for selecting one of these reaction modules for MNA applications at a specific site, depending on the contaminant group or groups that are present. In the case where chloroethenes only are present, the selection also depends on whether there is enough information and a desire to explicitly model the link between geochemical oxidation/reduction conditions and dechlorination. For MNA/EA sites, chloroethene reductive dechlorination using substrate/biomass-dependent reaction rates or cometabolic dechlorination can be selected to model the impact of substrates and electron donors on dechlorination. The RT3D reaction modules in Figure 14 are briefly described in Table 5 and are described in detail in Johnson and Truex [2006].

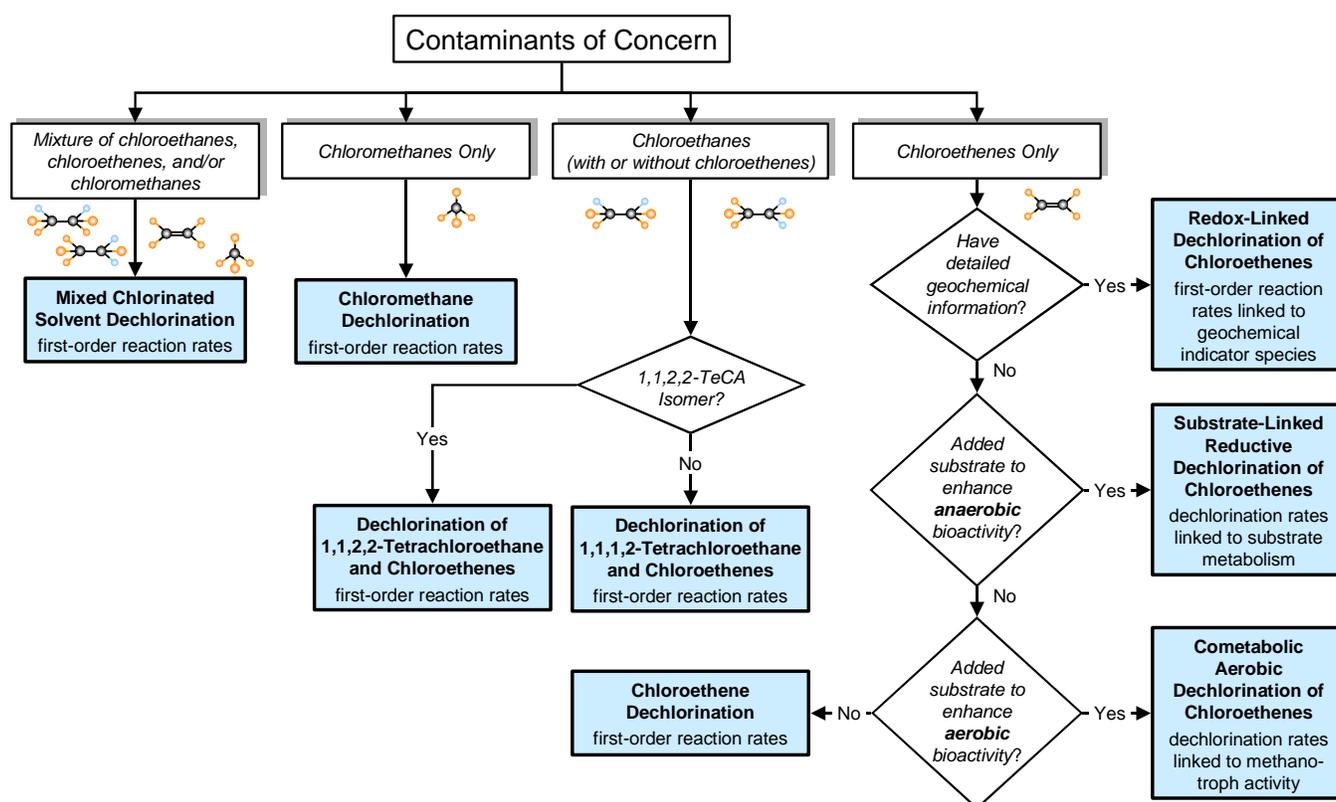


Figure 14. Flowchart for Selection of RT3D Reaction Modules for MNA/EA

Table 5. Description of the RT3D Reaction Modules for MNA/EA

Reaction Module Name	Reaction Module Description
Mixed Chloroethene/ Chloroethane/ Chloromethane Dechlorination	Dechlorination of a mixture of chloroethene, chloroethane, and chloromethane compounds using first-order rate expressions. This reaction module includes aerobic anoxic/anaerobic, and abiotic reactions.
Chloromethane Dechlorination	Dechlorination of chloromethane compounds using first-order rate expressions. This reaction module includes aerobic anoxic/anaerobic, and abiotic reactions.
Dechlorination of 1,1,2,2-Tetrachloroethane and Chloroethenes	Dechlorination of 1,1,2,2-tetrachloroethane and chloroethenes using first-order rate expressions. Includes 1,1,2-TCA and 1,2-DCA. This reaction module includes aerobic anoxic/anaerobic, and abiotic reactions.
Dechlorination of 1,1,1,2-Tetrachloroethane and Chloroethenes	Dechlorination of 1,1,1,2-tetrachloroethane and chloroethenes using first-order rate expressions. Includes 1,1,1-TCA and 1,1-DCA. This reaction module includes aerobic anoxic/anaerobic, and abiotic reactions.
Chloroethene Dechlorination	Dechlorination of chloroethene compounds using first-order rate expressions. All DCE isomers are included and additional pathways are represented over those in other similar RT3D reaction modules. This module includes aerobic and anoxic/anaerobic reactions (abiotic reactions are negligible for chloroethenes).
Redox-Linked Dechlorination of Chloroethenes	Dechlorination of chloroethene compounds using first-order rate expressions. This module includes aerobic and anoxic/anaerobic reactions, where the rate of these reactions is controlled by the oxidation/reduction conditions in the aquifer. Oxygen, nitrate, iron, sulfate/sulfide, and methane are used as indicator compounds to define the geochemical conditions. The user may choose to fix the spatial distribution of the geochemical indicator concentrations or allow the geochemical indicator compounds to undergo oxidation/reduction to give a time-varying spatial distribution of geochemical conditions. Note that this module does not perform full geochemical equilibrium calculations, but uses indicator species to assess redox conditions.
Substrate-Linked Reductive Dechlorination of Chloroethenes	Reductive dechlorination of chloroethene compounds using substrate/biomass-dependent reaction rates. The rates of dechlorination reactions are dependent on substrate (lactate) consumption and microbial growth. This is an Enhanced Attenuation reaction module.
Cometabolic Aerobic Dechlorination of Chloroethenes	Cometabolic dechlorination of TCE, DCE isomers, and VC by methanotrophic bacteria. The rate of dechlorination is dependent on the rate of methane consumption and microbial growth. This is an Enhanced Attenuation reaction module.

For each reaction module in Table 5, the user determines which reactions are active and provides the appropriate rate coefficients for the reactions. The user sets rate coefficients and/or stoichiometric yields to zero for inactive reactions. Reaction parameters can be spatially variable. For instance, if multiple geochemical settings are identified within the model domain, the rate coefficients in one area can be set to different values than for another area.

RT3D includes two other existing reaction modules potentially of interest to modelling for MNA. These existing reaction modules are not included in Table 5 because they are less detailed. The “Sequential First-Order Decay” and “Aerobic/Anaerobic PCE/TCE Dechlorination” reaction modules were designed for chloroethene dechlorination reactions. The former reaction module is a simple sequential reductive dechlorination module with all DCE isomers lumped as one species and no aerobic or abiotic reactions. While the latter reaction module is similar, but adds aerobic reactions and also tracks chloride as a chemical species. The reaction modules in Table 5 are recommended for application of RT3D simulation to a MNA evaluation, but there may be cases where the simpler reaction modules will suffice.

As mentioned in Section 5.0, additional mechanisms (e.g., non-equilibrium adsorption) or combinations of processes may be assembled in a user-defined reaction module. A user-defined reaction module can be created by writing a Fortran subroutine, possibly using an existing reaction module as a template. The process for developing a user-defined reaction module is described in the RT3D manual [Clement, 1997]. The user-defined reaction module is an extremely flexible tool for combining processes or for adding reaction kinetics for an entirely new set of chemicals (e.g., PCBs or pesticides).

8.0 Using a Reaction Module

Applying a reaction module typically requires 1) an understanding of the site with respect to the reaction processes that may be occurring, 2) appropriately configuring the model with respect to the reaction parameters and inputs that affect the reactions, 3) calibration of the model, and 4) conducting a matrix of simulations that address the modelling objectives for the site to the satisfaction of the stakeholders (e.g., site owners, regulators, technical review). This section describes each of these steps with respect to implementing a reaction module in RT3D.

8.1 Understanding Site Characteristics With Respect To Reaction Processes That May Be Occurring

The primary activities associated with identifying what reaction processes may be occurring, and therefore how the site should be modelled, involve assessing the site geochemistry and looking for reaction “signatures”. Section 6.0 describes the potential types of reactions that can occur based on categorizing the site into one of three basic geochemical settings. All of the site may fit within one of these settings, or there may be different geochemical settings associated with different portions or segments of the site (e.g., near source versus downgradient areas). The following process of categorizing geochemical setting of the site or site segment is based on the approach used in the *Scenarios Evaluation Tool for Chlorinated Solvent MNA* [Truex et al., 2006]. Table 6 summarizes the criteria used to identify the geochemical setting. All criteria listed in Table 6 for a geochemical category must generally be satisfied for selection of the geochemical setting. The criteria statements and numeric values should not be used as absolute rules. Technical judgment and knowledge of site conditions should be applied in conjunction with these guidelines when determining the site geochemical setting.

Based on the geochemical setting for the site or a segment of the site, the dechlorination reaction information in Section 6.0 can be consulted to determine what reactions may be occurring. For each reaction, specific intermediate and final dechlorination products are produced. These compounds can be used to identify specific reaction signatures for a site and assist in selecting the reactions that should be modelled. Once the set of reactions for a site have been identified, a specific reaction module can be selected based on the module information presented in Section 7.0.

Table 6. Criteria for Selecting the Geochemical Setting

Geochemical Setting	Description ¹
Anaerobic	Average dissolved oxygen concentration < ~1 mg/L (if meter) or < ~0.5 mg/L (if test kit); AND Sulfate concentration < ~ 50 mg/L; (value applies to most but not all sites) AND Nitrate < ~1 mg/L; AND Methane OR ferrous iron OR sulfide must be detected in most of the wells; AND TOC > ~5 mg/L AND Dechlorination daughter products must be present in the plume
Anoxic	Average dissolved oxygen concentration < ~2 mg/L (by meter or by test kit); AND Plume doesn't meet all of the anaerobic indicators
Aerobic	Average dissolved oxygen concentration > ~2 mg/L (by meter or by test kit); AND Plume doesn't meet ANY of the anaerobic indicators

¹ Criteria values are for guidance only and technical judgment related to specific site conditions should be used in applying these criteria.

8.2 Model Configuration

Once an appropriate reaction package has been selected, the model must be configured properly to use in fate and transport simulations. Configuration of the model with respect to the reaction processes includes 1) determining the appropriate reaction parameter values, 2) determining whether the reaction parameter values need to be spatially variable (e.g., are there multiple zones within the model that will have different reaction processes/rates), and 3) testing/calibration of the reaction module. The following sections discuss these configuration steps.

8.2.1 Determining Reaction Parameter Values

Determining the appropriate reaction parameter values to use in the reaction module is one of the most important steps in configuring a fate and transport model. Rate parameter values for hydrolysis reactions are generally not site specific for sites with near neutral pH conditions and literature values can be directly used for these parameters. However, most reaction parameters, such as the first order rate coefficients for biologically catalyzed reactions and the stoichiometric dechlorination yield, are highly site specific and it is typically not appropriate to use a generic parameter value to apply a reaction module for a specific site. The rate coefficient is dependent on the microbial ecology and geochemistry of the individual site. Likewise, the microbial

ecology and geochemistry effect the stoichiometric dechlorination yield (e.g., the moles of cis-1,2-DCE and trans-1,2-DCE produced from dechlorination of a mole of TCE). The scientific literature provides guidance about the likely range for these reaction parameter values, but a specific value appropriate to the each site must typically be selected. Site-specific reaction parameters are used for deterministic modelling. Alternatively, stochastic modelling can be applied, but site-specific ranges for parameter values should still be established.

There are several methods available to select a specific reaction parameter value for a specific site. Laboratory microcosm tests can be useful for selecting reaction parameter values because it is not always possible to determine the type of dechlorination attenuation process occurring at a site based on field data. While laboratory studies cannot exactly replicate field conditions, they can approximate field conditions and provide insight into the dechlorination attenuation mechanisms. Absolute rates of attenuation from laboratory studies are typically not expected to represent absolute rates under field conditions (except for some abiotic reactions). However, relative rates, for instance, for parent and daughter product dechlorination and the extent of dechlorination, can be reasonably approximated from laboratory data. Because of the controlled experimental conditions, detailed data analysis to determine the reaction pathways and rates is possible and provides useful information in terms of these relative dechlorination rates. Using this information, the laboratory rates can be adjusted during model calibration to match the available site data.

There are also field tests such as “push-pull” testing that can be used to assess reaction rates under *in situ* conditions [e.g., Kim et al., 2004]. These tests are similar to laboratory microcosm testing in that the reactions are measured based on the response observed to some specific experimental conditions. However, because the tests are conducted in the field, some of the experimental variables cannot be controlled as tightly as for a laboratory test. This type of testing should be considered for sites where the hydraulic and geochemical conditions are expected to enable sufficient control of the experiments for quantifying the reaction rates.

In a limited number of situations, direct analysis of contaminant concentration data from monitoring wells can be used to quantify reaction parameter values [e.g. U.S. EPA, 2002]. If a sufficient amount of spatial and temporal data is available, inverse modelling techniques as part of model calibration can be used to determine reaction rates. In this method, history matching is used to define the reaction rates that are then used to conduct predictive simulations for determining the future fate and transport of contaminants. In some cases, this type of inverse modelling is combined with information from laboratory microcosm tests or the literature to provide additional confidence in the results.

As an alternative to deterministically determining site-specific reaction parameter values, a range of parameter values can be used within a stochastic simulation process (e.g., a Monte Carlo approach) to address the fate and transport of contaminants in a probabilistic manner.

8.2.2 Determining Whether the Reaction Parameter Values Need to be Spatially Variable

Some sites may have uniform geochemical conditions and a single set of reaction parameters is sufficient to describe reactions for the fate and transport analysis. However, some hydrologic conditions and contaminant distributions lead to variations in geochemical conditions across a site that may induce different types of reactions or different rates of reactions. There are two approaches for addressing this type of variation.

A standard approach for addressing variability in reaction rates/processes is to use the variable reaction parameter function of RT3D and to set up zones within the model (e.g., blocks of grid cells) that have specific reaction parameter values. For instance, one zone may have anaerobic reactions active (e.g., near a source) and a downgradient zone may have aerobic reactions active because site data shows an increase in the dissolved oxygen concentration in this downgradient zone. To implement this approach, the modeler must examine the available geochemical and contaminant data and determine if specific zones of reactions can be identified. The model can then be configured with the appropriate parameter values for each zone.

A less common approach, due to the requirement for a significant amount of data and knowledge of the reaction processes, is to use a reaction module that varies the contaminant transformation rates based on the concentrations of selected geochemical indicators. RT3D offers one reaction module for chloroethene dechlorination based on the concentrations of geochemical indicators. In this module, a simplified geochemical approach (versus a full geochemical model) is used to define the reaction conditions (e.g., aerobic versus anaerobic and the dominant redox conditions) and the corresponding dechlorination behavior. Data for the geochemical indicators can be used to define (e.g., through interpolation) a specific indicator concentration for each of the grid cells such that the model will calculate contaminant transformation rates based on this imposed static distribution of geochemistry data. This approach provides a continuous spatial variability of the reaction rates based on the static spatial distribution of the geochemical indicators. The geochemical indicators can also be allowed to react and change over time if there is sufficient data available to define these rates of reactions. See Johnson and Truex [2006] for details on the reaction module implementing this type of geochemical indicator approach to dechlorination.

8.2.3 Module Testing/Calibration

Before proceeding to calibration of the full fate and transport model, it is important to test and calibrate the reaction module. The preceding sections discuss configuring the module based on the site conditions and data available for setting reaction parameters. It is typically useful to run the reaction module in a batch (no flow) mode or with a very simple flow model (e.g., on a simple testing grid with uniform hydraulic and transport conditions) to examine the simulated variation in the constituent concentrations over time and compare these patterns to what is expected based on the available data. In the case where laboratory microcosm tests have been conducted, batch simulations can be used to refine the reaction parameter values and calibrate

the module to the microcosm data. If less detailed data are available, the testing simulation results can still be examined with respect to the pattern of dechlorination and whether the relative persistence of the expected intermediate compounds matches the basic patterns observed at the site. While this task may seem duplicative to calibration of the full model, it is important to isolate the reaction module functioning so that any problems, including simple user input errors, can be more readily identified. It can be much more difficult to identify issues with the reaction module parameter values when advection, dispersion, and sorption are occurring at the same time within the full fate and transport model.

8.3 Model Calibration

When configuring the model, estimates of parameter values for the transport equation terms are established. In many cases, these estimates provide a reasonable range for the value of parameters, but cannot identify a specific correct value for a given site condition. The calibration process is used to seek the best fit of simulation results to a set of observed data available for the site. In this way, the calibration assesses the adequacy of the model in simulating the actual processes at the site. If the model meets expectations for the calibration, a technical basis for use of the model in a predictive mode has been established. Multiple statistically determined simulation scenarios can also be used to produce a range of model outputs for evaluation in contrast to interpretations of a best-fit model output.

To calibrate the model, parameters need to be varied within the acceptable range established in the model configuration and the model results compared to field data. This can be a directed process whereby the modeler sequentially varies parameters to converge on a best-fit solution, based on minimizing the difference between the model output and the field data. Care must be taken in this approach to consider that there may not be a unique set of parameters that define the best fit. However, with appropriate technical judgment, a reasonable best-fit model can be obtained. It is important to examine the parameter values that comprise the best-fit model to determine whether they make sense and to assess the impact of any parameters in the model that do not have a good physical basis (i.e., fitting factors). Prior to use of the model, the technical basis for the model fit needs to be assessed. A sensitivity assessment of the selected parameter values and the impact on the fit of the model is one means to evaluate whether the best fit has been obtained or whether predictive simulations should be conducted using several model configurations rather than just one best fit. It is also possible to use computer optimization routines to conduct the parameter variation testing and determine the best fit by comparison of the model to field data. This process, termed inverse modelling, requires that the comparison can be effectively described in terms of an objective function that the optimization routine can use to assess the suitability of parameter values. Further discussion of the calibration process, comparison to observed data, sensitivity analysis, and inverse modelling is available in a number of documents [e.g., ASTM, 1993; ASTM, 1994; ASTM, 1996; Hill, 1998; U.S. ACE, 1999; Neuman and Wierenga, 2003; Poeter et al., 2005].

Calibration of a flow model is typically achieved by variation of the relevant parameters (e.g., the hydraulic conductivity distribution) to match hydraulic head data for the site. Calibration of the flow model precedes calibration of the transport model, but may need to be iteratively adjusted during on the transport model calibration process. Typically, the calibration of the transport model is more difficult because there are more parameters that can impact the results and there are more data for the comparison (e.g., concentrations for multiple contaminant species). Standard groundwater interface packages provide techniques to aid in the calibration process.

8.4 MNA Modelling

Interpretation of model results is dependent on the context of how the modelling is being applied. This section discusses model interpretation as it applies to the identified roles of modelling for MNA. The two basic categories for interpretation of modelling results include 1) evaluating the impact of each attenuation process on migration of the plume, and 2) estimating whether the remedy (i.e., MNA or MNA/EA) will meet the remediation goals.

Numerical models have the computational ability to estimate the interaction of multiple processes temporally and spatially for scenarios that would be difficult to assess with analytical methods. Thus, numerical models can provide information to help analyze the relative importance of different fate and transport processes at an individual site. Using a model, multiple simulations can be conducted with variations in the input parameters. By comparing the results of these simulations, the relative importance of specific processes can be assessed. This modelling approach can be implemented with simple single parameter variation or using a statistical approach such as the Monte Carlo process.

Predictive simulations are used to estimate future plume migration under the selected remediation scenario (e.g., MNA/EA) and thereby assess the ability of this remedy to meet remediation goals. In some cases, it is appropriate to select specific simulation scenarios and use the calibrated model to assess whether remediation goals will be met under these selected conditions. Alternatively, the modelling approach may include conducting a statistical series of simulations (e.g., Monte Carlo analysis) to predict the probability for future contaminant distributions.

To aid in interpretation of modelling results, simulation data can be displayed a number of different ways. These display options include 1) concentration contours, 2) transect profiles, 3) time profiles, 4) probability contours for set concentration/risk values, and 5) probability of exceeding a limit at a set Point of Compliance. By conducting multiple simulations of different scenarios, models can provide information to evaluate the relative impact of each scenario in terms of how the output described above is changed and to evaluate the sensitivity of the results to changes in specific parameter values. The results of multiple simulations can be interpreted to assess the uncertainty of the modelling results; that is, assessing how variations in input

parameter data impact the model results. This uncertainty is important to consider in evaluating whether additional characterization for model input parameters is needed or to evaluate the technical risk of a decision based on the model results for the given level of information about the model inputs and the model configuration/calibration.

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Attachment 2:

**RT3D Reaction Modules for Natural and Enhanced Attenuation of
Chloroethanes, Chloroethenes, Chloromethanes, and Daughter
Products**



**Pacific Northwest
National Laboratory**

Operated by Battelle for the
U.S. Department of Energy

**RT3D Reaction Modules for Natural and
Enhanced Attenuation of Chloroethanes,
Chloroethenes, Chloromethanes, and
Daughter Products**

C. D. Johnson
M. J. Truex

July 2006



Prepared for
the U.S. Department of Energy
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**RT3D Reaction Modules for Natural and Enhanced
Attenuation of Chloroethanes, Chloroethenes,
Chloromethanes, and Daughter Products**

C. D. Johnson
M. J. Truex

July 2006

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Pacific Northwest National Laboratory
Richland, Washington 99352

Summary

This document describes a suite of Monitored Natural Attenuation/Enhanced Attenuation (MNA/EA) reaction modules that were developed for addressing complex chlorinated solvent reactions using the RT3D numerical solute transport code. As an introduction, an overview of these MNA/EA reaction modules is presented, including discussions of similarities between reaction modules, the purpose of key reaction parameters, and important considerations for using the reaction modules. Subsequent sections provide the details of the reaction kinetics (conceptual model and equations), data input requirements, and example (batch reactor) results for each reaction module. This document does not discuss reaction module implementation or validation; such information will accompany the software in the form of release notes or a supplement to the RT3D manual.

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1.0 Introduction

Monitored Natural Attenuation (MNA) is an environmental management strategy that relies on a variety of attenuation processes to destroy, transform, or immobilize contaminants and is implemented at appropriate sites by demonstrating that contaminant plumes have low risk and are either stable or shrinking. Numerical modelling can be one component of an assessment of MNA or Enhanced Attenuation (EA) (i.e., if MNA is not a viable single remedy). Numerical reactive transport modelling provides a tool with which to quantify the relative stability of a contaminant plume, particularly in cases where simpler evaluations are not suitable because of complex hydrology, past activity at the site, multiple contaminant sources, and/or complex reaction of multiple species. Selection of an appropriate model configuration to represent spatial and temporal variations in site-specific attenuation processes can facilitate assessment of the contaminant loading and attenuation capacity (i.e., mass balance) at the site.

RT3D is a numerical code for simulating three-dimensional multi-species reactive transport in groundwater for a user-configured site model [Clement, 1997; Clement et al., 1998; Clement and Johnson, 2002; Johnson et al., 2006]. RT3D can provide information to help analyze the relative importance of different fate and transport processes at an individual site and assess the plume in terms of a mass balance approach. A RT3D model can also be used to estimate the future fate and transport of contaminants. These predictions can be valuable input, along with other site information, in making timely decisions regarding implementation of remedial actions or for planning monitoring activities. A key function of the predictive capability of models is to estimate whether the remedy will meet the remediation goals when this determination cannot be made directly with field data.

The RT3D code solves a system of reactive transport equations for the tracked chemical species using an operator-split strategy to uncouple the advection, dispersion, source/sink mixing, and reaction terms of the governing transport equations [Johnson and Truex, 2006]. These separate terms are encapsulated in so-called "Packages," which delineate portions of the code as well as the required data input. RT3D improved on the publicly available MT3D code (whose more recent versions go by the name MT3DMS [Zheng and Wang, 1999]) by entirely replacing the Reaction Package code. The Reaction Package for RT3D is structured such that the reaction terms split off from the transport equations can be assembled into a reaction module comprised of a set of coupled ordinary differential equations (ODEs). Multiple reaction modules are defined within the RT3D code, with each reaction module encapsulating a set of kinetic equations that describe reaction of specific contaminants. Different approaches for describing contaminant degradation or transformation may be implemented for the same contaminants in different reaction modules.

RT3D versions 1.0 and 2.5 [Clement, 1997; Clement and Johnson, 2002] included a set of general-purpose reaction modules, including BTEX degradation (kinetic and instantaneous), rate-limited sorption, double Monod kinetics, and two simple chlorinated ethene reaction

modules. Additionally, RT3D has the ability to apply any user-defined reaction kinetics. While this user-defined option provides a means to employ more complex chlorinated solvent reaction kinetics, practitioners may not take advantage of this approach for two primary reasons. Users that configure an RT3D model through the graphical interface of a groundwater modelling software package may overlook the potential of the user-defined reaction module option if that option is absent in the graphical interface. Secondly, even when practitioners are aware of the user-defined reaction module option, they may view it as intimidating because it involves writing and compiling Fortran code.

This document describes a suite of MNA/EA reaction modules that were developed for addressing complex chlorinated solvent reactions using RT3D. As an introduction, an overview of these MNA/EA reaction modules is presented, including discussions of similarities between reaction modules, the purpose of key reaction parameters, and important considerations for using the reaction modules. Subsequent sections provide the details of the reaction kinetics (conceptual model and equations), data input requirements, and example (batch reactor) results for each reaction module. This document does not discuss reaction module implementation or validation; such information will accompany the software in the form of release notes or a supplement to the RT3D manual [Clement, 1997].

1.1 Overview of MNA/EA Reaction Modules

Eight RT3D reaction modules were developed for modelling complex chlorinated solvent reaction kinetics as part of evaluating MNA or EA. These eight modules are applicable for simulation of reactive transport of the chlorinated solvent chemicals listed in Table 1. Figure 1 shows the basic decision process for selecting one of these reaction modules for use in assessing MNA applications at a specific site, depending on the contaminant group or groups that are present. In the case where only chloroethenes are of concern, the selection also depends on whether there is enough information and a desire to explicitly model a link between geochemical oxidation/reduction conditions and dechlorination. For MNA/EA sites, chloroethene reductive dechlorination using substrate/biomass-dependent reaction rates or cometabolic aerobic dechlorination can be selected to model the impact of biostimulation on dechlorination. Table 2 summarizes the purpose of the RT3D reaction modules (both the existing ones and those described in this document). Table 2 also lists the total number of chemical species that are tracked, the number of constituents that are in the mobile aqueous phase (versus attached to the immobile soil phase), and the number of reaction parameters required for each reaction module.

Table 1. Chlorinated Contaminant Species Grouped by Contaminant Type

	Abbreviation	Contaminant Name (Synonyms)	Chemical Formula	CAS RN ^a	Molecular Weight ^b (g/mol)
Chloroethenes	PCE	Tetrachloroethene (Tetrachloroethylene, Perchloroethene)	$\text{CCl}_2=\text{CCl}_2$	127-18-4	165.8334
	TCE	Trichloroethene (Trichloroethylene)	$\text{CHCl}=\text{CCl}_2$	79-01-6	131.38834
	1,2-cis-DCE	cis-1,2-Dichloroethene (cis-1,2- Dichloroethylene, cis-DCE, c-DCE)	$\text{CHCl}=\text{CHCl}$	156-59-2	96.94328
	1,2-trans-DCE	trans-1,2-Dichloroethene (trans-1,2-Dichloroethylene, trans-DCE, t-DCE)	$\text{CHCl}=\text{CHCl}$	156-60-5	96.94328
	1,1-DCE	1,1-Dichloroethene (1,1-Dichloroethylene)	$\text{CCl}_2=\text{CH}_2$	75-35-4	96.94328
	VC	Chloroethene (Vinyl Chloride, Chloroethylene)	$\text{CH}_2=\text{CHCl}$	75-01-4	62.49822
Chloroethanes	1,1,2,2-TeCA	1,1,2,2-Tetrachloroethane	$\text{CHCl}_2-\text{CHCl}_2$	79-34-5	167.84928
	1,1,2-TCA	1,1,2-Trichloroethane (Vinyl Trichloride)	$\text{CH}_2\text{Cl}-\text{CHCl}_2$	79-00-5	133.40422
	1,2-DCA	1,2-Dichloroethane (Ethane Dichloride)	$\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$	107-06-2	98.95916
	1,1,1,2-TeCA	1,1,1,2-Tetrachloroethane	$\text{CHCl}-\text{CCl}_3$	630-20-6	167.84928
	1,1,1-TCA	1,1,1-Trichloroethane	CH_3-CCl_3	71-55-6	133.40422
	1,1-DCA	1,1-Dichloroethane	$\text{CH}_3-\text{CHCl}_2$	75-34-3	98.95916
	CA	Chloroethane (Ethyl Chloride)	$\text{CH}_3-\text{CH}_2\text{Cl}$	75-00-3	64.5141
Chloromethanes	CT	Tetrachloromethane (Carbon Tetrachloride)	CCl_4	56-23-5	153.8227
	CF	Trichloromethane (Chloroform)	CHCl_3	67-66-3	119.3776
	DCM	Dichloromethane (Methylene Dichloride, Methylene Chloride)	CH_2Cl_2	75-09-2	84.93258
	CM	Chloromethane (Methyl Chloride)	CH_3Cl	74-87-3	50.48752

^a CAS = Chemical Abstracts Service (see <http://www.cas.org/EO/regsys.html>)

^b Based on International Union of Pure and Applied Chemistry values reported by Loss [2003].

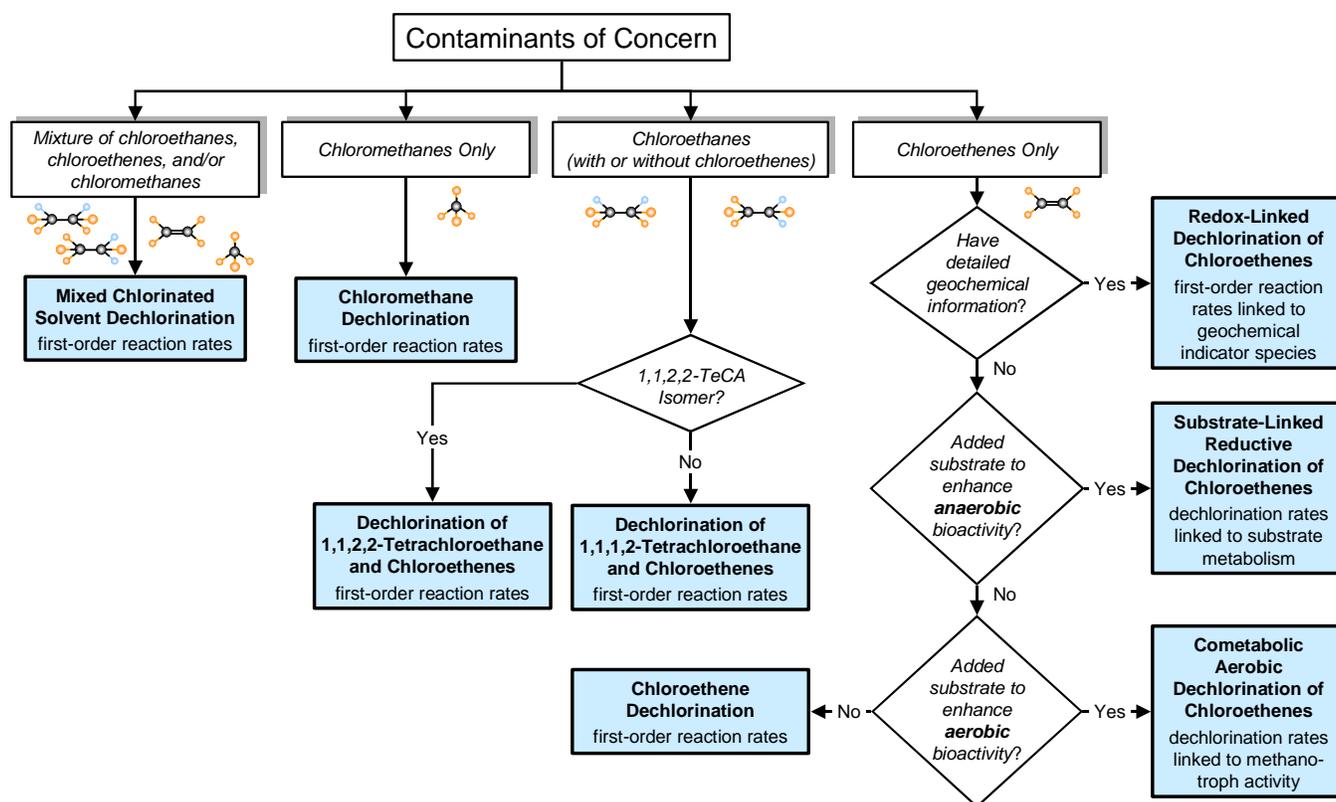


Figure 1. Flowchart Depicting the Logic for Selection of RT3D MNA/EA Reaction Modules Based on the Contaminant(s) Present, What Data is Available, and the MNA/EA Scenario under Consideration

Table 2. Summary of RT3D Reaction Modules (Existing and New)

Existing ^a	RT3D Reaction Module	Brief Description / Purpose	NCOMP (MCOMP) ^b	Number of Reaction Parameters ^c
◆	No Reaction	Simulation of non-reactive tracer.	user specified	0
◆	Two-Species Instantaneous Reactions	Instantaneous stoichiometric consumption of electron donor (e.g. hydrocarbon) and electron acceptor (e.g., oxygen) in each transport time step. BIOPLUME-II type reactions.	2 (2)	1
◆	Six Species, First-Order, Rate-Limited, BTEX Degradation using Sequential Electron Acceptors	First-order degradation of electron donor (e.g., BTEX) under up to six electron acceptor regimes, each with it's own reaction rate. Electron acceptors are utilized in a sequential manner in the order of O ₂ , NO ₃ ⁻ , Fe ²⁺ , SO ₄ ²⁻ , and CO ₂ (i.e., oxygen is the preferred electron acceptor until it is consumed, then the nitrate regime controls, and so on).	6 (6)	21

Table 2. (contd)

Existing ^a	RT3D Reaction Module	Brief Description / Purpose	NCOMP (MCOMP) ^b	Number of Reaction Parameters ^c
◆	Rate-Limited Sorption	Sorption is represented as a mass transfer-limited process that is a function of a mass transfer rate and the concentration driving force between aqueous and adsorbed phases. Equilibrium adsorption should not be used concurrently with this reaction module. No degradation is included in this reaction module, only the rate-limited sorption.	2 (1)	2
◆	Double Monod Model	Reaction between an electron donor and an electron acceptor that is mediated by actively growing and decaying bacteria. Bacteria are present in both aqueous and soil phases, where transfer between phases is based on first-order kinetic expressions. No specific microscopic biomass structure is assumed, and diffusional limitations across any soil phase biofilm are neglected. Permeability and porosity changes caused by bacterial growth are not accounted for in this reaction module.	4 (3)	8
◆	Sequential First-Order Decay	Sequential degradation reactions for up to 4 chemical species using first-order reaction kinetics (e.g., PCE → TCE → DCE → VC).	4 (4)	7
◆	Aerobic/Anaerobic PCE/TCE Dechlorination	Degradation of chlorinated ethenes (PCE, TCE, DCE, and VC) via both aerobic and anaerobic pathways, which are described with first-order reaction kinetics.	6 (6)	9
◆	User-Defined Kinetics	User-specified reaction kinetics. Any suitable/appropriate reaction kinetics may be described and implemented with this reaction module using the approach described in the RT3D manual [Clement, 1997].	user specified; limited to 100 species	user specified; limited to 100 parameters
	Mixed Chloroethene/ Chloroethane/ Chloromethane Dechlorination	Dechlorination of a mixture of chloroethene, chloroethane, and chloromethane compounds using first-order rate expressions. This reaction module includes aerobic, anoxic/anaerobic, and abiotic reactions.	18 (18)	53
	Chloromethane Dechlorination	Dechlorination of chloromethane compounds using first-order rate expressions. This reaction module includes aerobic, anoxic/anaerobic, and abiotic reactions.	5 (5)	9
	Dechlorination of 1,1,2,2-Tetrachloroethane and Chloroethenes	Dechlorination of 1,1,2,2-tetrachloroethane and chloroethenes using first-order rate expressions. Includes 1,1,2-TCA and 1,2-DCA. This reaction module includes aerobic, anoxic/anaerobic, and abiotic reactions.	11 (11)	35

Table 2. (contd)

Existing ^a	RT3D Reaction Module	Brief Description / Purpose	NCOMP (MCOMP) ^b	Number of Reaction Parameters ^c
	Dechlorination of 1,1,1,2-Tetrachloroethane and Chloroethenes	Dechlorination of 1,1,1,2-tetrachloroethane and chloroethenes using first-order rate expressions. Includes 1,1,1-TCA and 1,1-DCA. This reaction module includes aerobic, anoxic/anaerobic, and abiotic reactions.	11 (11)	28
	Chloroethene Dechlorination	Dechlorination of chloroethene compounds using first-order rate expressions. All DCE isomers are included and additional pathways are represented (as compared to the Aerobic/Anaerobic PCE/TCE Dechlorination reaction module). This module includes aerobic and anoxic/anaerobic reactions (abiotic reactions are negligible for chlorinated ethenes).	7 (7)	16
	Redox-Linked Dechlorination of Chloroethenes	Dechlorination of chloroethene compounds using first-order rate expressions. This module includes aerobic and anoxic/anaerobic reactions, where the rate of these reactions is controlled by the oxidation/reduction conditions in the aquifer. Oxygen, nitrate, iron, sulfate/sulfide, and methane are used as indicator compounds to define the geochemical conditions. The user may choose to fix the spatial distribution of the geochemical indicator concentrations or allow the geochemical indicator compounds to undergo oxidation/reduction to give a time-varying spatial distribution of geochemical conditions.	15 (14)	39
	Substrate-Linked Reductive Dechlorination of Chloroethenes	Reductive dechlorination of chloroethene compounds using substrate/biomass-dependent reaction rates. The rates of dechlorination reactions are dependent on substrate (lactate) consumption and microbial growth.	15 (12)	44
	Cometabolic Aerobic Dechlorination of Chloroethenes	Cometabolic dechlorination of TCE, DCE isomers, and VC by methanotrophic bacteria. The rate of dechlorination is dependent on the rate of methane consumption and microbial growth.	8 (6)	18

^a These reaction modules (marked with a ♦) were available beginning with RT3D version 1.0 [Clement, 1997].

^b NCOMP is the total number of chemical compounds that are tracked and MCOMP is the number of chemical compounds that are mobile (aqueous phase species).

^c Reaction parameters must all be of the same type, with either a constant value for all spatial locations or with a variable distribution through the spatial domain.

Five of the RT3D MNA/EA reaction modules represent the dechlorination reaction pathways for various mixtures of chlorinated ethenes, chlorinated ethanes, and chlorinated methanes. The complex network of biological and abiotic reaction pathways that are represented in these modules are depicted in Figure 2. The five reaction modules represent (1) the full reaction pathway network, (2) the chlorinated methanes only, (3) the 1,1,2,2-TeCA/PCE contaminant families, (4) the 1,1,1,2-TeCA/PCE contaminant families, and (5) the chlorinated ethenes only. The reaction network does not include heterogeneous abiotic reactions or abiotic reactions with half-lives of more than 200 years. Because these reaction modules target MNA conditions, cometabolism pathways (aerobic or anaerobic) are also not included.

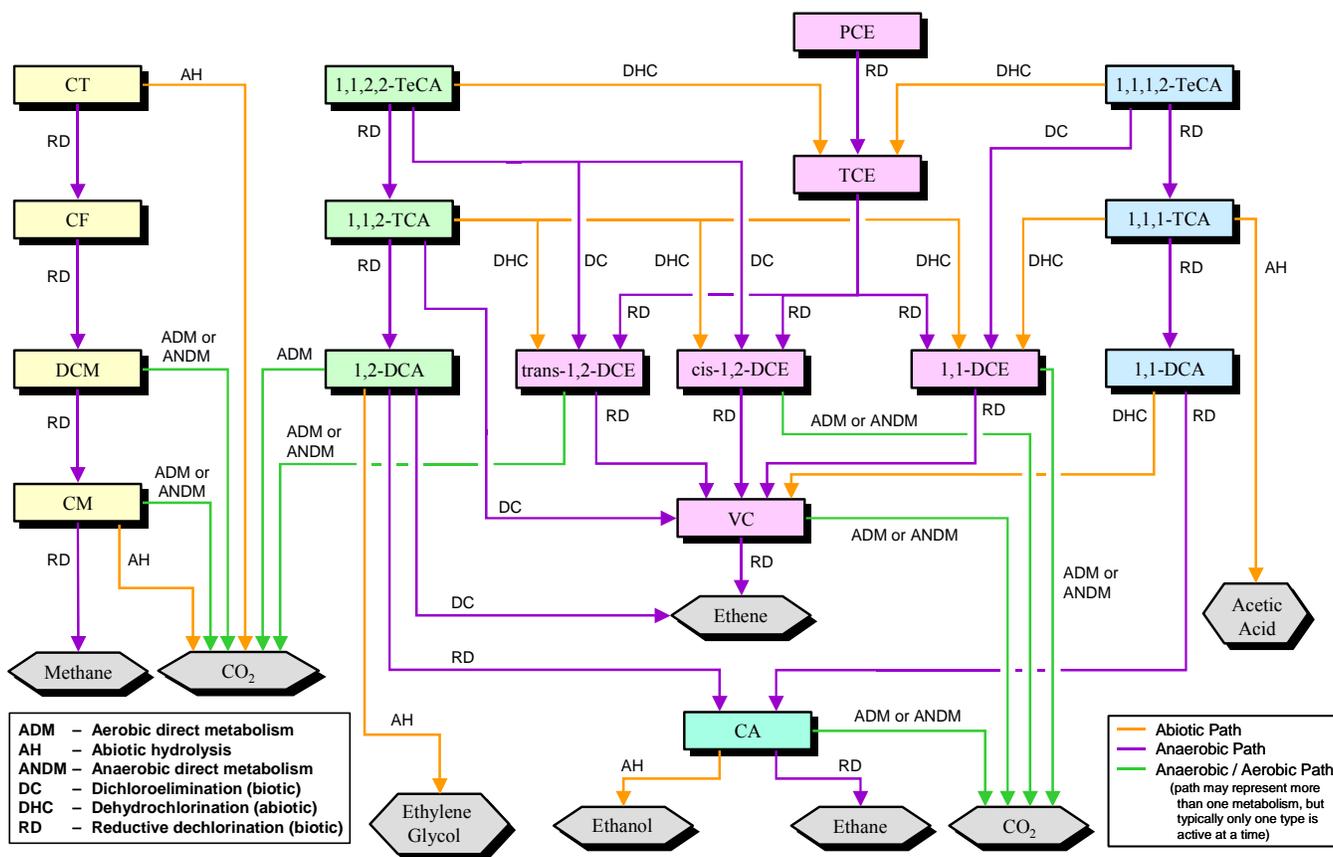


Figure 2. Reaction Pathway Network for Chlorinated Ethenes, Ethanes, and Methanes — Heterogeneous abiotic reactions, abiotic pathways with a half-life greater than 200 years, and cometabolic reaction pathways are not included.

Aerobic, anoxic, and anaerobic biological reaction pathways/conditions are all represented using first-order rate expressions. Table 3 describes the types of reaction processes that are noted for the pathways in Figure 2. The spatial distribution of a degradation regime (i.e., aerobic, anoxic, anaerobic, etc.) is delineated via user-specified zones within the RT3D model [e.g., Johnson et al., 2003a; Clement et al., 2000]. Reaction rates should be defined for each zone to represent the

expected microbial activity of that zone. The relevant reactions for a specific site (as determined by the user) may include all or some of the reaction pathways available in a reaction module. In zones where a reaction pathway is inactive, the spatially variable rate coefficient (and/or stoichiometric yield) is set to zero. For instance, an aerobic zone may have aerobic rate coefficients set to some appropriate value, while in the same zone the rate coefficients for anaerobic reactions would be zero. These five reaction modules also include first-order rate expressions for the abiotic degradation reactions shown in Figure 2.

Table 3. Descriptions of Biological and Abiotic Dechlorination Reactions

Reaction	Abbreviation	Description of Reaction
Aerobic Direct Metabolism	ADM	Use of the chlorinated compound as an electron donor for aerobic metabolism.
Anaerobic Direct Metabolism	ANDM	Use of the chlorinated compound as an electron donor for anaerobic respiration – typically coupled to iron reduction.
Abiotic Hydrolysis	AH	Homogeneous abiotic dechlorination as an initial reaction step – no specific reaction for this classification. The primary end product of this pathway is shown, omitting intermediate reaction steps.
Dichloroelimination (vicinal reduction)	DC	Dechlorination of a compound where the compound is used as an electron acceptor, the bacteria may or may not gain energy by reduction of the compound. This reaction removes two chloride atoms in an elimination reaction. The more general term for this reaction is dihaloelimination.
Dehydrochlorination	DHC	This reaction removes one chloride atom and one proton in an elimination reaction. This reaction is usually referred to as abiotic, but studies indicate that the reaction can be enhanced/catalyzed by bacteria [e.g., Maymó-Gatell et al., 1999] and/or minerals (e.g., clay) [e.g., Cervini-Silva et al., 2003]. The more general term for this reaction is dehydrohalogenation. Sometimes this type of reaction is referred to as dehydrodehalogenation.
Reductive Dechlorination (hydrogenolysis)	RD	Dechlorination of a compound where the compound is used as an electron acceptor, the bacteria may or may not gain energy by reduction of the compound. This reaction removes one chloride atom from the compound and replaces it with a proton.

As an alternative to defining fixed spatial zones of activity, a reaction module is provided for first-order dechlorination of chlorinated ethenes by natural attenuation processes where the pathways and rates of transformation are dependent on the oxidation-reduction (redox) conditions. In the presence of oxygen, the reaction module allows aerobic dechlorination of DCE isomers and VC to occur. However, the presence of oxygen or nitrate inhibits the anoxic/anaerobic dechlorination pathways of the reaction module. At low oxygen concentrations, the dominant redox condition for the reaction module is determined based on the concentrations of the three key redox couples: iron (ferrous iron/amorphous ferric hydroxide),

sulfur (sulfate/sulfide), and methane (methane/CO₂). Note that this reaction module does not perform full geochemical equilibrium calculations, but provides a simplified framework to represent the oxidation-reduction conditions in the aquifer. Tracking the redox conditions based on the oxygen, nitrate, iron, sulfur, and methane geochemical indicator species allows the user to model a continuum of reaction regimes whose spatial extent may vary over time as the redox conditions change. Alternately, this reaction module can use a fixed (temporally constant) spatial distribution of dechlorination activity that is defined based on the initial concentrations for the geochemical indicator species.

This redox-dependant reaction module is founded on the assumption that the redox conditions (determined from the key redox couples) control the dechlorination reaction rate. Based on the premise that degradation under natural attenuation conditions occurs as a result of the activity of a widely distributed and essentially constant low concentration population of indigenous bacteria, this reaction module does not track microbial growth. The bacterial species that are active, and hence the rate at which dechlorination occurs, is assumed to be dependent on the geochemical conditions. If sufficient substrate is present at a site to drive bacterial growth dynamics, other reaction modules that consider biomass growth and subsequent impacts to dechlorination rate (e.g., substrate-linked dechlorination) should be used.

Two reaction modules are provided for enhanced attenuation (or accelerated *in situ* bioremediation). Biostimulation through addition of a readily fermentable substrate is a common approach to increase the dechlorination rates. The substrate-linked reaction module provides a method for modelling the biodegradation rate of chlorinated ethenes as a function of the amount of biomass that grows on the supplied substrate. The substrate is represented by lactate, which may be fermented to propionate, acetate, and hydrogen by fermenting bacteria. Methanogenic bacteria, growing on acetate and hydrogen, drive the reductive dechlorination of the chlorinated ethenes in this reaction module. Because the anaerobic dechlorination reaction rates are linked to the microbial population, the rates are inherently based on a spatially variable continuum. Aerobic direct metabolism of DCE and VC is represented using first-order rate expressions

The other enhanced attenuation RT3D reaction module is aerobic cometabolism of chlorinated ethenes (excluding PCE). Cometabolic chlorinated ethene degradation in this reaction module is dependent on the concentration of the chlorinated ethene compound and the concentration of methanotrophic bacteria, is inhibited by methane, requires oxygen, and deactivates biomass (i.e., the module indirectly accounts for destruction of the monooxygenase enzyme by the chlorinated ethene degradation intermediate epoxide compounds). Methanotroph biomass growth occurs in response to the availability of methane and oxygen. As with the substrate-linked reaction module, the dechlorination reaction rates are implicitly spatially variable because of the dependence on the biomass concentration.

1.2 RT3D MNA/EA Reaction Module Commonalities

Although the MNA/EA reaction modules discussed in this document represent different reaction kinetics, they share certain common features/concepts. These common features are presented in this section.

Every MNA/EA reaction module described in this document is configured for chemical species concentrations in units of mg/L, although the actual kinetic equations are typically based on moles instead of mass. Reaction parameters are requested in convenient units and are internally converted to a molar basis where required.

All of these MNA/EA reaction modules include a conservative tracer as one of the tracked chemical species. This allows the user to assess non-reactive transport without completing a separate model configuration and simulation run. Information on the transport of a conservative tracer can be useful, for example, in the calibration of a model or in assessing "what if" scenarios.

Transformation/degradation reactions of the contaminants (biotic and abiotic) are assumed to occur only for the aqueous phase (dissolved) contaminant mass in all of these MNA/EA reaction modules. Thus, there is no degradation of the sorbed contaminant. This is a conservative assumption in terms of being protective of groundwater receptors. If sorbed-phase contaminant mass is actually degraded for a particular site, then these reaction modules will under predict the rate of mass loss, resulting in a longer transport distance and a longer remediation timeframe (depending on the extent of contaminant partitioning to the soil). Modifications to these reaction modules could be completed to provide a user-defined reaction module that explicitly tracks sorbed-phase contaminants and allows the sorbed phase contaminants to be degraded. Note that this assumption of reaction only for dissolved phase contaminant mass does not imply anything about the nature of the microbial population mediating the degradation (i.e., it does not imply that only aqueous phase microbes act on contaminants while attached microbes do nothing). However, the two Enhanced Attenuation reaction modules explicitly track microbial biomass as attached (immobile) constituents, ignoring the effects of any free-living (suspended) bacteria. While not included in these reaction modules, the impact of attached versus free-living bacteria is an area of ongoing research [e.g., Harvey and Barber, 1992; Holm et al., 1992; Doong et al., 1997; Lehman et al., 2001; Yolcubal et al., 2002; Painter et al., 2005] that could be explored through a user-defined reaction module.

For internal program consistency, the reaction parameters for these MNA/EA reaction modules must be specified in a model configuration as being either all spatially constant or all spatially variable. To implement spatial variability, reaction parameters are allowed to vary within the full 3D reactive transport model domain on a grid cell by grid cell basis.

These RT3D MNA/EA reaction modules provide a framework for modelling the reaction kinetics at a particular site. Site-specific knowledge from field data and/or laboratory tests should be applied to determine an appropriate model configuration for reaction parameter values. In the absence of site-specific information, generic data or ranges of values from the open literature may be acceptable, but the potential impact of such non-site-specific data on the model output should be discussed.

1.3 Discussion of Select Reaction Parameters

Stoichiometric dechlorination yields and reaction rate constants are reaction parameters that are used throughout the MNA/EA reaction modules. Other reaction parameters (such as Monod half saturation constants, inhibition constants, etc.) are more specific to the kinetic formulations of particular reaction modules. The document sections for individual reaction modules include information on all reaction parameters required for that reaction module, but the more common kinds of reaction parameters are described here to give a general sense of the purpose of the parameters.

Stoichiometric dechlorination yields are used in the reaction kinetics to represent the mole fraction of a product (daughter species) produced for every mole of reactant (parent) species transformed by a specific process (i.e., anaerobic dechlorination or abiotic degradation). Stoichiometric yields are constrained to sum up to 1.0 for reaction of a given parent species by a particular type of process. Note however, that some stoichiometric yield values may not be included as a user-specified reaction parameter because the daughter species (e.g., CO₂) is not explicitly tracked. While all pathways in Figure 2 are possible, some may not occur at a particular site, in which case the stoichiometric dechlorination yield is assigned a value of zero for the inactive pathway. Truex et al. [2002a] provide an example (in a user-defined reaction module) where reductive dechlorination pathways for 1,1,2,2-TeCA and 1,1,2-TCA were not included because those pathways were not observed in microcosm tests with site sediment and groundwater. In cases where there is only one reaction pathway (e.g., reductive dechlorination of PCE to TCE), the stoichiometric dechlorination yield is fixed internal to the reaction module at a value of 1.0 (i.e., the value cannot be altered by the user in the model configuration).

As an example of stoichiometric dechlorination yields, consider dechlorination of 1,1,2-TCA, which may be dechlorinated by both anaerobic and abiotic processes. Table 4 shows the calculated stoichiometric dechlorination yields for a scenario in which a total of 1.5 moles of 1,1,2-TCA are transformed to daughter products in the stated amounts (columns 1 and 2). This type of data (used to determine the stoichiometric dechlorination yield) is typically collected from site-specific microcosms or from literature data. For a microcosm test, the stoichiometric dechlorination yields would be determined along with the site-specific reaction rates by adjusting parameters to fit microcosm data from multiple experiments (i.e., differing conditions, not just replicates).

Table 4. Example of Stoichiometric Dechlorination Yield Resulting From Transformation of 1.5 Moles of 1,1,2-TCA

Daughter Species	Moles Produced ^a	Reaction Type ^b	Calculated Stoichiometric Dechlorination Yield (mol/mol)	Comments
cis-DCE	0.36	abiotic (AE)	$Fab_{cDCE/112TCA} = 0.6$	Sum of Yields equals 100%
trans-DCE	0.24	abiotic (AE)	$Fab_{tDCE/112TCA} = 0.4$	
1,1-DCE	0.0	abiotic (AE)	$Fab_{11DCE/112TCA} = 0.0$	
1,2-DCA	0.18	anaerobic (RD)	$Fan_{12DCA/112TCA} = 0.2$	Sum of Yields equals 100%
VC	0.72	anaerobic (DC)	$Fan_{VC/112TCA} = 0.8$	
Total Moles: 1.5				

^a These are purely arbitrary numbers for use in this example.

^b See Table 3 for a list of reaction types and abbreviations.

As with the stoichiometric dechlorination yields, the reaction rates are generally site specific, although abiotic reaction rates may tend to be more consistent from site to site. Abiotic reaction rates are primarily dependent on the temperature and pH of the groundwater, while biotic reaction rates are a function of the microbial population and geochemical setting. Many of the reactions in these reaction modules assume that the biological (and abiotic) dechlorination rates can be modeled as first-order processes, implying that the biomass concentration stays constant and electron donor concentration is low (both reasonable assumptions for a MNA site). See the section on the Mixed Chloroethene/Chloroethane/Chloromethane Dechlorination reaction module for further discussion of first-order reaction kinetics.

Dechlorination rates for reactant species are determined from the overall rate at which the compound is decaying under defined conditions, coupled with the amounts of product species that are produced. Field data may be used to determine reaction rates, depending on the history of site activities and how well the subsurface is understood in terms of groundwater flow, dispersion, and adsorption. Laboratory microcosm data from multiple experiments with differing initial conditions can be used to fit the reaction rate parameters and the stoichiometric dechlorination yields. Laboratory microcosm experiments with site sediment and groundwater are useful to examine the reaction kinetics without the convoluting influences of contaminant transport processes (e.g., advection and dispersion). Typically the resultant set of reaction rate parameter values from this calibration against microcosm data will be higher than the rates seen in the field because of differences in the soil/water ratio, temperature, and the disturbed/undisturbed nature of the sediment. However, it may be reasonable to assume that the relative rates of different reaction processes (e.g., the rate of CT transformation relative to the

rate of CF transformation) consistent between the laboratory and the field. It is then necessary as part of the calibration process for the full three-dimensional reactive transport model to estimate if and what magnitude of a correction factor between the laboratory-derived rates and the rates in the field is required.

Several reaction modules use Monod half saturation constants (e.g., K_s) and/or inhibition coefficients (e.g., k_{is}) in the functional forms shown in Equations 1 and 2 for Monod and inhibition terms, respectively. The constants represent the point in a hyperbolic curve where the ordinate has a value of 0.5. Figure 3 shows example curves (with arbitrary data) for a Monod term and an inhibition term, both with constants of 5.0. These terms are used as multipliers on the kinetic equations regarding bacterial growth rate or dechlorination rate. The Monod term is typically used to account for nutrient limitations – as the concentration of a nutrient decreases, the rate of reaction will decrease. Conversely, the inhibition term restricts the rate of reaction as the concentration of an inhibiting species increases. Lu et al. [1999] provide an example usage of these types of terms for modelling BTEX biodegradation.

$$\text{Monod Term} \Rightarrow \frac{[\text{Species}]}{K_s + [\text{Species}]} \quad (1)$$

$$\text{Inhibition Term} \Rightarrow \frac{k_{is}}{k_{is} + [\text{Species}]} \quad (2)$$

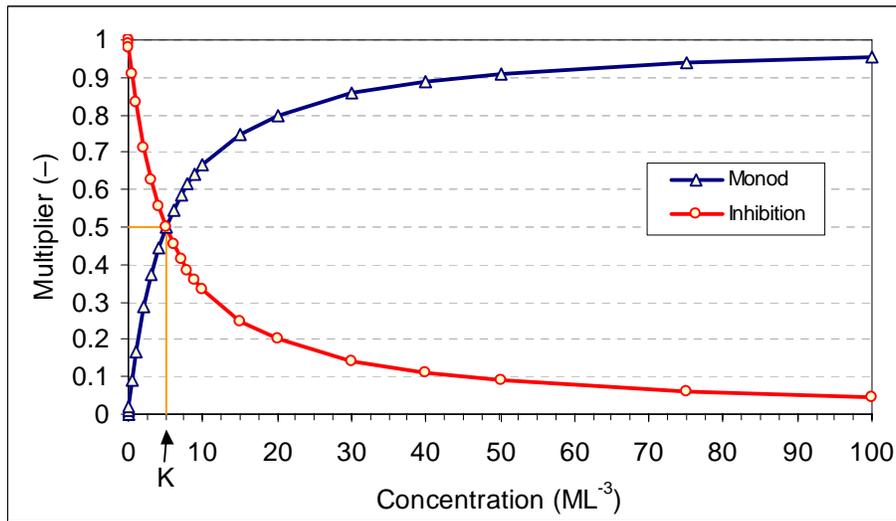


Figure 3. Arbitrary Examples of the Curves Obtained for Monod and Inhibition Terms — These terms are typically used as multipliers on the reaction rate to account for nutrient limitations and inhibition effects, respectively.

Reaction parameters may be defined as spatially constant or spatially variable, depending on site conditions and the available information. For instance, if multiple geochemical settings (as discussed in Johnson et al. [2006]) are identified within the model domain, the parameters in one area can be set to different values than for another area. Reaction parameter values can vary spatially because of differences in geochemistry (e.g., concentrations/types of electron acceptors, anaerobic/anoxic/aerobic setting), temperature, substrate availability, and microbial population (in terms of both numbers of bacteria and types of bacteria). Field-scale geochemical data can be used to assign spatially variable reaction rates to account for variations in biological activity resulting from differences in, for example, substrate or electron acceptor concentrations. Alternately, laboratory microcosm data from different areas of a site may suggest different reaction rates/processes.

Where a reaction pathway is inappropriate for a given spatial location, the dechlorination rate and/or the stoichiometric dechlorination yield for that pathway can be set to zero. Alternately, a specific location may exhibit the reaction pathway, but at a slower rate than another location. Figure 4 shows an example of a reactive transport model having four different reaction zones. In this example, the "Anaerobic Zone-1" has a high anaerobic dechlorination rate and no aerobic reactions occur, "Anaerobic Zone-2" has a lower anaerobic dechlorination rate and no aerobic reactions occur, the "Transition Zone" has a low rates for both anaerobic and aerobic processes, and in the "Aerobic Zone" there is a high rate of aerobic dechlorination and zero anaerobic dechlorination. See Clement et al. [2000] and Johnson et al. [2003a] for examples of applying this zonal approach to specifying reaction parameter values for reactive transport models of actual field sites.

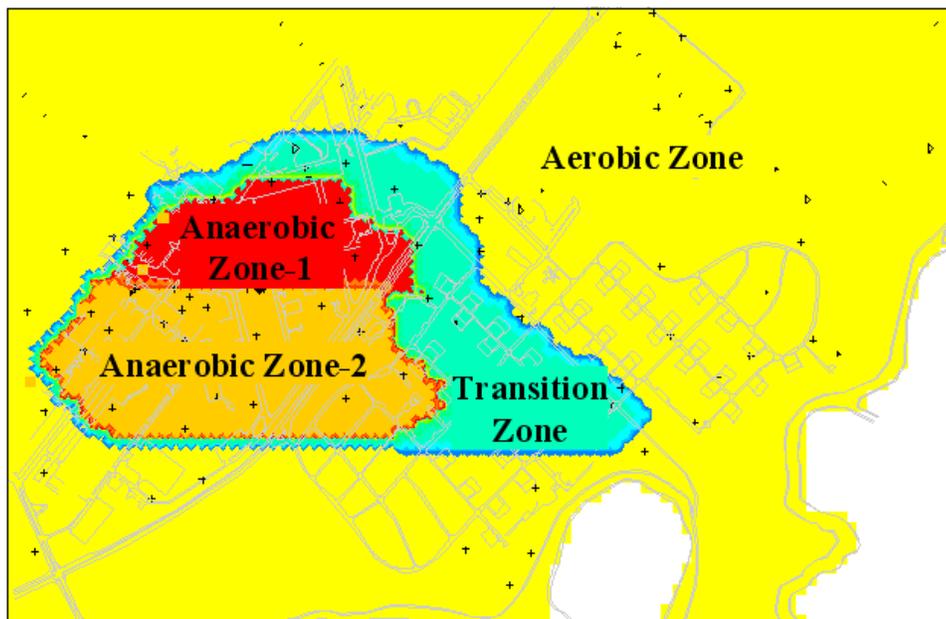


Figure 4. *Example of a Reactive Transport Model Having Multiple Reaction Zones, Each with Differing Reaction Parameter Values — Figure adapted from Clement et al. [2000].*

1.4 Important Considerations for Using the RT3D MNA/EA Reaction Modules

The RT3D MNA/EA reaction modules described in this document were developed to provide ready access to more complex reaction scenarios that may be of interest for monitored natural attenuation or enhanced attenuation modelling evaluations. Each of these reaction modules has a clearly stated set of kinetic expressions and associated reaction parameters that incorporate certain assumptions and define one specific approach to representing the stated scenario. In some ways, these reaction modules were designed to provide flexibility in modelling potential complex reaction kinetics. For example, the Dechlorination of 1,1,2,2-Tetrachloroethane and Chloroethenes reaction module includes many reaction pathways, but some number of those pathways may not be needed for a particular site while they are at yet another site. In other ways, the reaction modules represent specific conceptual models, such as the assumption of first-order kinetics (e.g., Mixed Chloroethene/Chloroethane/Chloromethane Dechlorination) or the linkage of dechlorination rates to the rate of methanogenesis (Substrate-Linked Reductive Dechlorination of Chloroethenes). The user should read this document and fully understand the scope of a given reaction module, including the assumptions and limitations corresponding to the conceptual model/approach. The approach taken here for a given reaction module is only one way of addressing a reaction scenario and may or may not be appropriate for any specific site. *It is incumbent on the practitioner to assess the suitability of any RT3D reaction module for a particular application. Additionally, testing and validation of the reaction modules is not included in this report and is the responsibility of the module user.*

The descriptions of the MNA/EA reaction modules are written to explain the kinetic expressions that are used in the modules and are in no way intended to imply or assert that these approaches are the "right" or "best" way to represent the reaction kinetics. However, the authors propose that these reaction modules may be useful for MNA/EA at some sites. Indeed, the authors have successfully used prototypes of several of these reaction modules at field sites. A prototype of the Dechlorination of 1,1,2,2-Tetrachloroethane and Chloroethenes reaction module was used to evaluate MNA for a multicomponent dissolved-phase contaminant plume at a National Priorities List site in Louisiana [Truex et al., 2002; Spencer et al., 2002]. Design of an anaerobic accelerated *in situ* bioremediation system at a U.S. Navy facility in California [Johnson et al., 1999; Leigh et al., 2000] was completed with a prototype of the Substrate-Linked Reductive Dechlorination of Chloroethenes reaction module. The rate of vinyl chloride degradation by anaerobic processes at this U.S. Navy facility was determined to be too slow for the site objectives, thus a prototype of the Cometabolic Aerobic Dechlorination of Chloroethenes reaction module was used to design an aerobic accelerated *in situ* bioremediation system [Truex et al., 2002b; Johnson et al., 2003b] for sequential anaerobic/aerobic treatment of the site.

In addition to prototype kinetic formulations, the basis of the MNA/EA reaction modules also included literature information and simplified conceptual models to describe the impact of complex processes such as geochemistry on dechlorination. The five RT3D MNA/EA reaction

modules using first-order reaction kinetic expressions to model dechlorination were configured based on a review of literature to define potential dechlorination reaction mechanisms [Johnson et al., 2006]. The literature review was not intended to be exhaustive, but provides examples of laboratory information that is available to describe the reaction pathways. In the Redox-Linked Dechlorination of Chloroethenes reaction module, the rate of dechlorination is adjusted based on a simplified framework to represent the oxidation-reduction conditions in the aquifer. This module enables the user to link dechlorination rate to the concentration of geochemical indicator species. The module is not a full geochemical model, but provides one potential means for the user to model dechlorination at sites where the oxidation-reduction conditions in the aquifer are spatially or temporally variable. While there are multiple ways to model substrate-linked reductive dechlorination, the Substrate-Linked Reductive Dechlorination of Chloroethenes reaction module specifically links the dechlorination rate to the activity of methanogenic bacteria, similar to Skeen et al. [1995]. The activity of methanogenic bacteria in this reaction module is dependent on the availability of acetate and hydrogen produced from the fermentation of lactate and propionate by other bacteria. The Cometabolic Aerobic Dechlorination of Chloroethenes reaction module uses kinetic expressions from the scientific literature [e.g., Semprini et al., 1991; Alvarez-Cohen and McCarty, 1991; Chang and Alvarez-Cohen, 1996] that describe the cometabolic degradation process with inhibition by methane and with the toxicity effect of the intermediate degradation product on the methanotrophic bacteria.

Example results representing reaction in a batch reactor are provided in this document for all of the MNA/EA reaction modules. These examples demonstrate that the expected behavior is observed under selected conditions. However, it was beyond the scope of the development effort to rigorously test these MNA/EA reaction modules and benchmark them against other numerical codes, analytical solutions, or existing field data. This exercise is left to the practitioner as part of the assessment whether these reaction modules are appropriate for a particular site. The authors intend that future efforts will address these testing and validation issues.

If the conceptual model and/or kinetic expressions of an RT3D reaction module are deemed insufficient or unsuitable for application at a given site, then the user has the option of writing a user-defined reaction module to provide the desired configuration of the kinetic expressions. The user may find that an existing reaction module can serve as a convenient starting point for making modifications. For example, additional reaction mechanisms/pathways that are not currently included in the Mixed Chloroethene/Chloroethane/Chloromethane Dechlorination reaction module may be identified in the future as valid degradation routes, and the Mixed Chloroethene/Chloroethane/Chloromethane Dechlorination reaction module could be supplemented with the new pathway(s) to form a user-defined reaction module. The RT3D manual [Clement, 1997] and version 2.5 update document [Clement and Johnson, 2002] provide information on assembling a user-defined reaction module. Alternately, the authors can be contacted for assistance in developing a new reaction module.

2.0 Mixed Chloroethene/Chloroethane/Chloromethane Dechlorination

2.1 Conceptual Model for Dechlorination Reactions

This reaction module describes dechlorination of chloroethanes, chloroethenes, chloromethanes, and related daughter products using first-order rate expressions. The module includes abiotic, aerobic, and anoxic/anaerobic reaction pathways, which the user may selectively turn off by setting the (spatially variable) values of the stoichiometric yields and/or the reaction rate constants to zero. See the section on RT3D MNA/EA Reaction Module Commonalities and the Discussion of Select Reaction Parameters for additional information on features common to all of these MNA/EA reaction modules and explanation of key reaction parameters.

Table 5 lists the chemical species included in this reaction module. Figure 5 shows the conceptual model describing the potential biotic and abiotic degradation pathways of both chlorinated ethene and chlorinated ethane contaminants.

The reaction pathways included in this reaction module are based on a review of literature on dechlorination reaction mechanisms for the chlorinated solvents of interest [Johnson et al., 2006]. The literature review was not intended to be exhaustive, but provides examples of laboratory information that is available to describe the reaction pathways. For convenience, a select set of references that discuss abiotic and biotic reaction pathways for chlorinated solvents are noted in this document [Mabey and Mill, 1978; Vogel et al., 1987; Jeffers et al., 1989; Washington, 1995; Chen et al., 1996; Jeffers et al., 1996; Jeffers and Wolfe, 1996; Lorah and Olsen, 1999; Truex et al., 2001; De Wildeman and Verstraete, 2003; Lorah and Voytek, 2004; Hunkeler et al., 2005]. To make this reaction module more flexible and general, several pathways that were not directly supported by laboratory data in the open literature are included (Table 6). The reaction network does not include heterogeneous abiotic reactions or abiotic reactions with half-lives of more than 200 years. Because this reaction module targets MNA conditions, non-contaminant substrate concentrations are assumed to be low enough that cometabolism pathways (aerobic or anaerobic) should not be included. If reaction mechanisms/pathways that are not currently included in this reaction module are identified as valid or important degradation routes, then such pathways could be included in a user-defined reaction module based on the Mixed Chloroethene/Chloroethane/Chloromethane Dechlorination reaction module.

Table 5. Chemical Species Included in the Mixed Chloroethene/Chloroethane/Chloromethane Dechlorination Reaction Module

No.	Abbreviation ^a	Chemical Name	Selected Alternate Name	CAS ^b Registry Number	Molecular Weight ^c (g/mol)	Chemical Formula
1	1122TeCA	1,1,2,2-Tetrachloroethane	1,1,2,2-TeCA	79-34-5	167.84928	C ₂ H ₂ Cl ₄
2	112TCA	1,1,2-Trichloroethane	Vinyl Trichloride; 1,1,2-TCA	79-00-5	133.40422	C ₂ H ₃ Cl ₃
3	12DCA	1,2-Dichloroethane	Ethane Dichloride; 1,2-DCA	107-06-2	98.95916	C ₂ H ₄ Cl ₂
4	CA	Chloroethane	Ethyl Chloride	75-00-3	64.5141	C ₂ H ₅ Cl
5	1112TeCA	1,1,1,2-Tetrachloroethane	1,1,1,2-TeCA	630-20-6	167.84928	C ₂ H ₂ Cl ₄
6	111TCA	1,1,1-Trichloroethane	1,1,1-TCA	71-55-6	133.40422	C ₂ H ₃ Cl ₃
7	11DCA	1,1-Dichloroethane	1,1-DCA	75-34-3	98.95916	C ₂ H ₄ Cl ₂
8	PCE	Tetrachloroethene	Tetrachloroethylene; Perchloroethylene	127-18-4	165.8334	C ₂ Cl ₄
9	TCE	Trichloroethene	Trichloroethylene	79-01-6	131.38834	C ₂ HCl ₃
10	cDCE	cis-1,2-Dichloroethene	cis-1,2-Dichloroethylene; cis-1,2-DCE; cis-DCE	156-59-2	96.94328	C ₂ H ₂ Cl ₂
11	tDCE	trans-1,2-Dichloroethene	trans-1,2-Dichloroethylene; trans-1,2-DCE; trans-DCE	156-60-5	96.94328	C ₂ H ₂ Cl ₂
12	11DCE	1,1-Dichloroethene	1,1-Dichloroethylene; Vinylidene Chloride; 1,1-DCE	75-35-4	96.94328	C ₂ H ₂ Cl ₂
13	VC	Chloroethene	Vinyl Chloride; Chloroethylene	75-01-4	62.49822	C ₂ H ₃ Cl
14	CT	Tetrachloromethane	Carbon Tetrachloride	56-23-5	153.82270	CCl ₄
15	CF	Trichloromethane	Chloroform	67-66-3	119.37764	CHCl ₃
16	DCM	Dichloromethane	Methylene Dichloride, Methylene Chloride	75-09-2	84.93258	CH ₂ Cl ₂
17	CM	Chloromethane	Methyl Chloride	74-87-3	50.48752	CH ₃ Cl
18	Tracer	Conservative Tracer	—	N/A	N/A	N/A

^a These abbreviations refer to the specific chemicals listed here and should not be confused with different chemicals that may use the same abbreviation in other reaction modules.

^b CAS = Chemical Abstracts Service (see <http://www.cas.org/EO/regsys.html>)

^c Based on International Union of Pure and Applied Chemistry values reported by Loss [2003].

N/A – Not Applicable

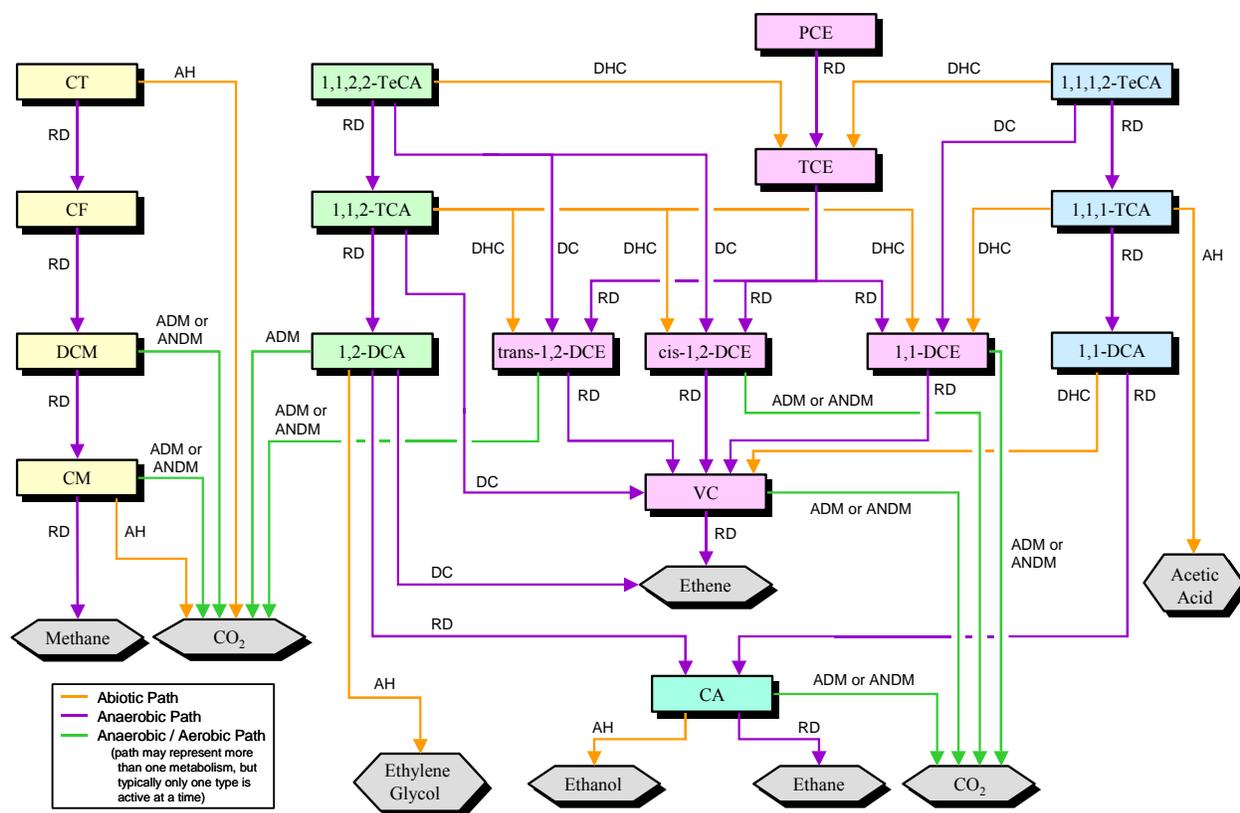


Figure 5. Conceptual Model for Dechlorination Reactions in the Mixed Chloroethene/Chloroethane/Chloromethane Dechlorination Reaction Module — Species in hexagonal shaded boxes are innocuous products and are not tracked in the reaction module. The reaction types for each pathway are described in Table 3.

Table 6. Reaction Pathways Without Laboratory Data in the Open Literature, but Which Are Included in the RT3D MNA/EA First-Order Reaction Modules

Reaction Pathway	Reaction Process	Comments
1,1-DCE → CO ₂	ANDM	Potential pathway because ANDM occurs for cis/trans-1,2-DCE.
CA → CO ₂	ADM	Probable, but not documented pathway based on ADM of VC.
CA → CO ₂	ANDM	Probable, but not documented pathway based on ANDM of VC.
1,1,1,2-TeCA → 1,1,1-TCA	RD	This pathway is listed as a presumptive degradation route in the literature review figures [Johnson et al., 2006] despite the lack of laboratory data in the open literature.
CM → CH ₄	RD	This pathway is listed as a presumptive degradation route in the literature review figures [Johnson et al., 2006] despite the lack of laboratory data in the open literature.

The kinetic relations for the reactions in this reaction module were developed by assuming that the dechlorination kinetics can be approximated as first-order reactions. Some previous studies have shown that first-order kinetics can be reasonable for modeling dechlorination mechanisms at field scales [e.g., U.S. EPA, 1998; Clement et al., 2000] and at low concentrations [Schmidt et al., 1985]. Yet other studies [e.g., Scow et al., 1986] have determined that first-order kinetics were not appropriate. A number of factors (substrate concentration, microbial population density, etc.) can impact the type of model (first-order, Monod, logistic, etc.) that best represents biodegradation of a chemical [Simkins and Alexander, 1984; Alexander, 1985; Schmidt et al., 1985]. The first-order assumption should be assessed [e.g., Bekins et al., 1998] as part of the determination of whether the reaction module is suitable for the intended application.

First-order kinetics express the biodegradation rates as being primarily a function of the concentration of the contaminant. Implicit to the assumption of first-order kinetics is that the microbial population is nongrowing, i.e., the substrate concentration is much less than the Monod half saturation constant. First-order kinetics do not have an explicit dependence on the type or concentration of electron donor, the type or quantity of bacteria present, nutrient limitations, or the geochemical conditions. All of these factors should be evaluated prior to selecting a first-order model to represent biodegradation. Additionally, this reaction module does not include a provision for inhibition by the contaminants; the contaminants are assumed to be present at less than inhibitory concentrations.

If a biostimulation or bioaugmentation technique is used at a site (increasing the quantity of subsurface bacteria) then the assumptions associated with first-order kinetics may not be valid and the user should apply something along the lines of one of the EA reaction modules.

2.2 Reaction Equations

The set of ODEs comprising this reaction module are shown in Equations 3 to 20. These ODEs describe the reaction kinetics for the 18 chemical species in Table 5. See Table 7 for a detailed itemization of all reaction parameters used in this reaction module.

$$\frac{dC_{1122TeCA}}{dt} = \left(-kan_{1122TeCA} \cdot C_{1122TeCA} - kab_{1122TeCA} \cdot C_{1122TeCA} \right) \quad (3)$$

$$\frac{dC_{1112TeCA}}{dt} = \left(-kan_{1112TeCA} \cdot C_{1112TeCA} - kab_{1112TeCA} \cdot C_{1112TeCA} \right) \quad (4)$$

$$\frac{dC_{112TCA}}{dt} = \left(Y_{\frac{112TCA}{1122TeCA}} \cdot Fan_{\frac{112TCA}{1122TeCA}} \cdot kan_{1122TeCA} \cdot C_{1122TeCA} - kan_{112TCA} \cdot C_{112TCA} - kab_{112TCA} \cdot C_{112TCA} \right) \quad (5)$$

$$\frac{dC_{1117CA}}{dt} = \left(\begin{array}{l} Y_{\frac{1117CA}{1112TeCA}} \cdot Fan_{\frac{1117CA}{1112TeCA}} \cdot kan_{1112TeCA} \cdot C_{1112TeCA} - kan_{1117CA} \cdot C_{1117CA} - kab_{1117CA} \cdot C_{1117CA} \end{array} \right) \quad (6)$$

$$\frac{dC_{12DCA}}{dt} = \left(\begin{array}{l} Y_{\frac{12DCA}{112TCA}} \cdot Fan_{\frac{12DCA}{112TCA}} \cdot kan_{112TCA} \cdot C_{112TCA} \\ - kan_{12DCA} \cdot C_{12DCA} - kab_{12DCA} \cdot C_{12DCA} - kae_{12DCA} \cdot C_{12DCA} \end{array} \right) \quad (7)$$

$$\frac{dC_{11DCA}}{dt} = \left(\begin{array}{l} Y_{\frac{11DCA}{1117CA}} \cdot kan_{1117CA} \cdot C_{1117CA} \\ - kan_{11DCA} \cdot C_{11DCA} - kab_{11DCA} \cdot C_{11DCA} \end{array} \right) \quad (8)$$

$$\frac{dC_{CA}}{dt} = \left(\begin{array}{l} Y_{\frac{CA}{12DCA}} \cdot Fan_{\frac{CA}{12DCA}} \cdot kan_{12DCA} \cdot C_{12DCA} + Y_{\frac{CA}{11DCA}} \cdot kan_{11DCA} \cdot C_{11DCA} \\ - kan_{CA} \cdot C_{CA} - kab_{CA} \cdot C_{CA} - kae_{CA} \cdot C_{CA} \end{array} \right) \quad (9)$$

$$\frac{dC_{PCE}}{dt} = \left(\begin{array}{l} - kan_{PCE} \cdot C_{PCE} \end{array} \right) \quad (10)$$

$$\frac{dC_{TCE}}{dt} = \left(\begin{array}{l} Y_{\frac{TCE}{PCE}} \cdot kan_{PCE} \cdot C_{PCE} + Y_{\frac{TCE}{1122TeCA}} \cdot kab_{1122TeCA} \cdot C_{1122TeCA} \\ + Y_{\frac{TCE}{1112TeCA}} \cdot kab_{1112TeCA} \cdot C_{1112TeCA} \\ - kan_{TCE} \cdot C_{TCE} \end{array} \right) \quad (11)$$

$$\frac{dC_{cDCE}}{dt} = \left(\begin{array}{l} Y_{\frac{DCE}{1122TeCA}} \cdot Fan_{\frac{cDCE}{1122TeCA}} \cdot kan_{1122TeCA} \cdot C_{1122TeCA} + Y_{\frac{DCE}{TCE}} \cdot Fan_{\frac{cDCE}{TCE}} \cdot kan_{TCE} \cdot C_{TCE} \\ + Y_{\frac{DCE}{112TCA}} \cdot Fab_{\frac{cDCE}{112TCA}} \cdot kab_{112TCA} \cdot C_{112TCA} \\ - kan_{cDCE} \cdot C_{cDCE} - kae_{cDCE} \cdot C_{cDCE} \end{array} \right) \quad (12)$$

$$\frac{dC_{iDCE}}{dt} = \left(\begin{array}{l} Y_{\frac{DCE}{112TeCA}} \cdot Fan_{\frac{iDCE}{112TeCA}} \cdot kan_{1122TeCA} \cdot C_{1122TeCA} + Y_{\frac{DCE}{TCE}} \cdot Fan_{\frac{iDCE}{TCE}} \cdot kan_{TCE} \cdot C_{TCE} \\ + Y_{\frac{DCE}{112TCA}} \cdot Fab_{\frac{iDCE}{112TCA}} \cdot kab_{112TCA} \cdot C_{112TCA} \\ - kan_{iDCE} \cdot C_{iDCE} - kae_{iDCE} \cdot C_{iDCE} \end{array} \right) \quad (13)$$

$$\frac{dC_{11DCE}}{dt} = \left(\begin{array}{l} Y_{\frac{DCE}{TCE}} \cdot Fan_{\frac{11DCE}{TCE}} \cdot kan_{TCE} \cdot C_{TCE} + Y_{\frac{DCE}{112TCA}} \cdot Fan_{\frac{11DCE}{112TCA}} \cdot kan_{112TCA} \cdot C_{112TCA} \\ + Y_{\frac{DCE}{111TCA}} \cdot Fab_{\frac{11DCE}{111TCA}} \cdot kab_{111TCA} \cdot C_{111TCA} \\ + Y_{\frac{DCE}{1112TeCA}} \cdot Fan_{\frac{11DCE}{1112TeCA}} \cdot kan_{1112TeCA} \cdot C_{1112TeCA} \\ - kan_{11DCE} \cdot C_{11DCE} - kae_{11DCE} \cdot C_{11DCE} \end{array} \right) \quad (14)$$

$$\frac{dC_{VC}}{dt} = \left(\begin{array}{l} Y_{\frac{VC}{112TCA}} \cdot Fan_{\frac{VC}{112TCA}} \cdot kan_{112TCA} \cdot C_{112TCA} + Y_{\frac{VC}{111TCA}} \cdot Fan_{\frac{VC}{111TCA}} \cdot kan_{111TCA} \cdot C_{111TCA} \\ + Y_{\frac{VC}{DCE}} \cdot Fan_{\frac{VC}{cDCE}} \cdot kan_{cDCE} \cdot C_{cDCE} \\ + Y_{\frac{VC}{DCE}} \cdot Fan_{\frac{VC}{iDCE}} \cdot kan_{iDCE} \cdot C_{iDCE} \\ + Y_{\frac{VC}{DCE}} \cdot Fan_{\frac{VC}{DCE11}} \cdot kan_{DCE11} \cdot C_{DCE11} \\ + Y_{\frac{VC}{11DCA}} \cdot kab_{11DCA} \cdot C_{11DCA} \\ - kan_{VC} \cdot C_{VC} - kae_{VC} \cdot C_{VC} \end{array} \right) \quad (15)$$

$$\frac{dC_{CT}}{dt} = \left(-kan_{CT} \cdot C_{CT} - kab_{CT} \cdot C_{CT} \right) \quad (16)$$

$$\frac{dC_{CF}}{dt} = \left(Y_{\frac{CF}{CT}} \cdot kan_{CT} \cdot C_{CT} - kan_{CF} \cdot C_{CF} \right) \quad (17)$$

$$\frac{dC_{DCM}}{dt} = \begin{pmatrix} \frac{Y_{DCM}}{CF} \cdot kan_{CF} \cdot C_{CF} \\ - kan_{DCM} \cdot C_{DCM} - kae_{DCM} \cdot C_{DCM} \end{pmatrix} \quad (18)$$

$$\frac{dC_{CM}}{dt} = \begin{pmatrix} \frac{Y_{CM}}{DCM} \cdot Fan_{\frac{CM}{DCM}} \cdot kan_{DCM} \cdot C_{DCM} \\ - kan_{CM} \cdot C_{CM} - kab_{CM} \cdot C_{CM} - kae_{CM} \cdot C_{CM} \end{pmatrix} \quad (19)$$

$$\frac{dC_{Tracer}}{dt} = 0.0 \quad (\text{Conservative [non-reactive] tracer.}) \quad (20)$$

The first-order decay rate constants [T^{-1}] of the i^{th} species are represented in the equations above by the kan_i , kae_i , and kab_i terms for anaerobic biological reactions, aerobic biological reactions, or abiotic reactions, respectively. The concentration of the i^{th} species is represented by the C_i term [ML^{-3}]. The R_i terms represent the retardation factor for the i^{th} species [unitless].

In cases where multiple daughter products may be produced from dechlorination of a single parent species, the amount of each daughter species that is produced is a function of a mass yield [MM^{-1}] and a stoichiometric dechlorination yield [mol/mol]. The mass yield value, $Y_{d/p}$, accounts for the difference in molecular weight between the parent species "p" and the daughter species "d." All isomers of a daughter chemical have the same mass yield. Mass yield values are included in the reaction module code and do not need to be input by the user. The stoichiometric dechlorination yield represents the site-specific stoichiometry for each reaction pathway that occurs as either an anaerobic ($Fan_{d/p}$) or an abiotic process ($Fab_{d/p}$). The stoichiometric dechlorination yield is the fractional moles of daughter species that are produced by dechlorination of one mole of the parent species. The net yield is the product of the mass yield and the stoichiometric dechlorination yield. To preserve the mass balance, the values of the stoichiometric dechlorination yields are constrained by the relations in Equations 21 to 31.

$$Fan_{\frac{112TCA}{1122TeCA}} + Fan_{\frac{cDCE}{1122TeCA}} + Fan_{\frac{iDCE}{1122TeCA}} = 1.0 \quad (21)$$

$$Fan_{\frac{111TCA}{1112TeCA}} + Fan_{\frac{11DCE}{1112TeCA}} = 1.0 \quad (22)$$

$$Fan_{\frac{12DCA}{112TCA}} + Fan_{\frac{YC}{112TCA}} = 1.0 \quad (23)$$

$$Fan_{\frac{cDCE}{TCE}} + Fan_{\frac{iDCE}{TCE}} + Fan_{\frac{11DCE}{TCE}} = 1.0 \quad (24)$$

$$Fab_{\frac{cDCE}{112TCA}} + Fab_{\frac{iDCE}{112TCA}} + Fab_{\frac{11DCE}{112TCA}} = 1.0 \quad (25)$$

$$Fab_{\frac{11DCE}{111TCA}} \leq 1.0 \quad (26)$$

$$Fan_{\frac{CA}{12DCA}} \leq 1.0 \quad (27)$$

$$Fan_{\frac{VC}{cDCE}} \leq 1.0 \quad (28)$$

$$Fan_{\frac{VC}{iDCE}} \leq 1.0 \quad (29)$$

$$Fan_{\frac{VC}{11DCE}} \leq 1.0 \quad (30)$$

$$Fan_{\frac{CM}{DCM}} \leq 1.0 \quad (31)$$

2.3 Required Input

The reaction parameters for this reaction module are made available to RT3D as part of the input for the Reaction Package. The Reaction Package input file structure is discussed in the RT3D manual and addendum [Clement, 1997; Clement and Johnson, 2002]. The 53 reaction parameters that must be specified for this reaction module are listed in Table 7 in the required order (ID Number) with units and a description. Site-specific knowledge from field data or laboratory tests should be applied to determine an appropriate model configuration for reaction parameters (i.e., the values and the spatial distribution).

Table 7. *Input Parameters for the Mixed Chloroethene/Chloroethane/Chloromethane Dechlorination Reaction Module*

ID #	Parameter	Fortran Variable	Units	Description
1	$Fab_{\frac{cDCE}{112TCA}}$	fab_cdce_tca2	mol/mol	Moles of cis-1,2-DCE produced from abiotic decay of one mole of 1,1,2-TCA
2	$Fab_{\frac{iDCE}{112TCA}}$	fab_tdce_tca2	mol/mol	Moles of trans-1,2-DCE produced from abiotic decay of one mole of 1,1,2-TCA
3	$Fab_{\frac{11DCE}{112TCA}}$	fab_11dce_tca2	mol/mol	Moles of 1,1-DCE produced from abiotic decay of one mole of 1,1,2-TCA

Table 7. (contd)

ID #	Parameter	Fortran Variable	Units	Description
4	$Fab_{\frac{11DCE}{111TCA}}$	fab_11dce_tca1	mol/mol	Moles of 1,1-DCE produced from abiotic decay of one mole of 1,1,1-TCA
5	$Fan_{\frac{112TCA}{1122TeCA}}$	fan_tca2_teca2	mol/mol	Moles of 1,1,2-TCA produced from anaerobic decay of one mole of 1,1,2,2-TeCA
6	$Fan_{\frac{cDCE}{1122TeCA}}$	fan_cdce_teca2	mol/mol	Moles of cis-1,2-DCE produced from anaerobic decay of one mole of 1,1,2,2-TeCA
7	$Fan_{\frac{tDCE}{1122TeCA}}$	fan_tdce_teca2	mol/mol	Moles of trans-1,2-DCE produced from anaerobic decay of one mole of 1,1,2,2-TeCA
8	$Fan_{\frac{12DCA}{112TCA}}$	fan_dca2_tca2	mol/mol	Moles of 1,2-DCA produced from anaerobic decay of one mole of 1,1,2-TCA
9	$Fan_{\frac{VC}{112TCA}}$	fan_vc_tca2	mol/mol	Moles of VC produced from anaerobic decay of one mole of 1,1,2-TCA
10	$Fan_{\frac{CA}{12DCA}}$	fan_ca_dca2	mol/mol	Moles of CA produced from anaerobic decay of one mole of 1,2-DCA
11	$Fan_{\frac{111TCA}{1112TeCA}}$	fan_tca1_teca1	mol/mol	Moles of 1,1,1-TCA produced from anaerobic decay of one mole of 1,1,1,2-TeCA
12	$Fan_{\frac{11DCE}{1112TeCA}}$	fan_11dce_teca1	mol/mol	Moles of 1,1-DCE produced from anaerobic decay of one mole of 1,1,1,2-TeCA
13	$Fan_{\frac{cDCE}{TCE}}$	fan_cdce_tce	mol/mol	Moles of cis-1,2-DCE produced from anaerobic decay of one mole of TCE
14	$Fan_{\frac{tDCE}{TCE}}$	fan_tdce_tce	mol/mol	Moles of trans-1,2-DCE produced from anaerobic decay of one mole of TCE
15	$Fan_{\frac{11DCE}{TCE}}$	fan_11dce_tce	mol/mol	Moles of 1,1-DCE produced from anaerobic decay of one mole of TCE
16	$Fan_{\frac{VC}{cDCE}}$	fan_vc_cdce	mol/mol	Moles of VC produced from anaerobic decay of one mole of cis-1,2-DCE
17	$Fan_{\frac{VC}{tDCE}}$	fan_vc_tdce	mol/mol	Moles of VC produced from anaerobic decay of one mole of trans-1,2-DCE
18	$Fan_{\frac{VC}{11DCE}}$	fan_vc_11dce	mol/mol	Moles of VC produced from anaerobic decay of one mole of 1,1-DCE
19	$Fan_{\frac{CM}{DCM}}$	fan_cm_dcm	mol/mol	Moles of CM produced from anaerobic decay of one mole of DCM
20	$kab_{1122TeCA}$	kab_teca2	1/day	First-order decay coefficient for abiotic dechlorination of 1,1,2,2-TeCA

Table 7. (contd)

ID #	Parameter	Fortran Variable	Units	Description
21	kab_{112TCA}	kab_tca2	1/day	First-order decay coefficient for abiotic dechlorination of 1,1,2-TCA
22	kab_{12DCA}	kab_dca2	1/day	First-order decay coefficient for abiotic dechlorination of 1,2-DCA
23	kab_{CA}	kab_ca	1/day	First-order decay coefficient for abiotic dechlorination of CA
24	$kab_{1112TeCA}$	kab_teca1	1/day	First-order decay coefficient for abiotic dechlorination of 1,1,1,2-TeCA
25	kab_{111TCA}	kab_tca1	1/day	First-order decay coefficient for abiotic dechlorination of 1,1,1-TCA
26	kab_{11DCA}	kab_dca1	1/day	First-order decay coefficient for abiotic dechlorination of 1,1-DCA
27	kab_{CT}	kab_ct	1/day	First-order decay coefficient for abiotic dechlorination of CT
28	kab_{CM}	kab_cm	1/day	First-order decay coefficient for abiotic dechlorination of CM
29	$kan_{1122TeCA}$	kan_teca2	1/day	First-order decay coefficient for anaerobic dechlorination of 1,1,2,2-TeCA
30	kan_{112TCA}	kan_tca2	1/day	First-order decay coefficient for anaerobic dechlorination of 1,1,2-TCA
31	kan_{12DCA}	kan_dca2	1/day	First-order decay coefficient for anaerobic dechlorination of 1,2-DCA
32	kan_{CA}	kan_ca	1/day	First-order decay coefficient for anaerobic dechlorination of CA
33	$kan_{1112TeCA}$	kan_teca1	1/day	First-order decay coefficient for anaerobic dechlorination of 1,1,1,2-TeCA
34	kan_{111TCA}	kan_tca1	1/day	First-order decay coefficient for anaerobic dechlorination of 1,1,1-TCA
35	kan_{11DCA}	kan_dca1	1/day	First-order decay coefficient for anaerobic dechlorination of 1,1-DCA
36	kan_{PCE}	kan_pce	1/day	First-order decay coefficient for anaerobic dechlorination of PCE
37	kan_{TCE}	kan_tce	1/day	First-order decay coefficient for anaerobic dechlorination of TCE
38	kan_{cDCE}	kan_cdce	1/day	First-order decay coefficient for anaerobic dechlorination of cis-1,2-DCE
39	kan_{tDCE}	kan_tdce	1/day	First-order decay coefficient for anaerobic dechlorination of trans-1,2-DCE
40	kan_{11DCE}	kan_11dce	1/day	First-order decay coefficient for anaerobic dechlorination of 1,1-DCE
41	kan_{VC}	kan_vc	1/day	First-order decay coefficient for anaerobic dechlorination of VC

Table 7. (contd)

ID #	Parameter	Fortran Variable	Units	Description
42	kan_{CT}	kan_ct	1/day	First-order decay coefficient for anaerobic dechlorination of CT
43	kan_{CF}	kan_cf	1/day	First-order decay coefficient for anaerobic dechlorination of CF
44	kan_{DCM}	kan_dcm	1/day	First-order decay coefficient for anaerobic dechlorination of DCM
45	kan_{CM}	kan_cm	1/day	First-order decay coefficient for anaerobic dechlorination of CM
46	kae_{12DCA}	kae_dca2	1/day	First-order decay coefficient for aerobic dechlorination of DCA
47	kae_{CA}	kae_ca	1/day	First-order decay coefficient for aerobic dechlorination of CA
48	kae_{cDCE}	kae_cdce	1/day	First-order decay coefficient for aerobic dechlorination of cis-1,2-DCE
49	kae_{tDCE}	kae_tdce	1/day	First-order decay coefficient for aerobic dechlorination of trans-1,2-DCE
50	kae_{11DCE}	kae_11dce	1/day	First-order decay coefficient for aerobic dechlorination of 1,1-DCE
51	kae_{VC}	kae_vc	1/day	First-order decay coefficient for aerobic dechlorination of VC
52	kae_{DCM}	kae_dcm	1/day	First-order decay coefficient for aerobic dechlorination of DCM
53	kae_{CM}	kae_cm	1/day	First-order decay coefficient for aerobic dechlorination of CM

2.4 Example Simulations

Simulations with this reaction module were conducted with RT3D in a batch reactor (no flow) mode to show examples of how the reaction module simulates the pattern of dechlorination. The parameter values for each example simulation are listed in Tables 8 through 11. These parameters are arbitrary values and are not directly related to any specific laboratory data. Site-specific values would need to be determined as part of a calibration process. Results for these example batch simulations are shown in Figures 6 through 9, respectively.

Table 8. *Parameter Values for Example Simulation 1 – Anaerobic Conditions – with the Mixed Chloroethene/Chloroethane/Chloromethane Dechlorination Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fab_cdce_tca2	0.2	mol/mol	28	kab_cm	0.000094	1/day
2	fab_tdce_tca2	0.7	mol/mol	29	kan_teca2	0.005	1/day
3	fab_11dce_tca2	0.1	mol/mol	30	kan_tca2	0.01	1/day
4	fab_11dce_tca1	0.2	mol/mol	31	kan_dca2	0.025	1/day
5	fan_tca2_teca2	0.2	mol/mol	32	kan_ca	0.025	1/day
6	fan_cdce_teca2	0.15	mol/mol	33	kan_teca1	0.005	1/day
7	fan_tdce_teca2	0.05	mol/mol	34	kan_tca1	0.01	1/day
8	fan_dca2_tca2	0.2	mol/mol	35	kan_dca1	0.025	1/day
9	fan_vc_tca2	0.8	mol/mol	36	kan_pce	0.025	1/day
10	fan_ca_dca2	0.2	mol/mol	37	kan_tce	0.025	1/day
11	fan_tca1_teca1	0.2	mol/mol	38	kan_cdce	0.025	1/day
12	fan_11dce_teca1	0.8	mol/mol	39	kan_tdce	0.025	1/day
13	fan_cdce_tce	0.8	mol/mol	40	kan_11dce	0.025	1/day
14	fan_tdce_tce	0.2	mol/mol	41	kan_vc	0.0025	1/day
15	fan_11dce_tce	0	mol/mol	42	kan_ct	0.005	1/day
16	fan_vc_cdce	0.8	mol/mol	43	kan_cf	0.0005	1/day
17	fan_vc_tdce	0.8	mol/mol	44	kan_dcm	0.005	1/day
18	fan_vc_11dce	0.8	mol/mol	45	kan_cm	0.005	1/day
19	fan_cm_dcm	0.5	mol/mol	46	kae_dca2	0	1/day
20	kab_teca2	0.006	1/day	47	kae_ca	0	1/day
21	kab_tca2	0.0015	1/day	48	kae_cdce	0	1/day
22	kab_dca2	0.00003	1/day	49	kae_tdce	0	1/day
23	kab_ca	0.001	1/day	50	kae_11dce	0	1/day
24	kab_teca1	0.006	1/day	51	kae_vc	0	1/day
25	kab_tca1	0.001	1/day	52	kae_dcm	0	1/day
26	kab_dca1	0.00005	1/day	53	kae_cm	0	1/day
27	kab_ct	0.000047	1/day				

Table 9. Parameter Values for Example Simulation 2 – Aerobic Conditions – with the Mixed Chloroethene/Chloroethane/Chloromethane Dechlorination Reaction Module

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fab_cdce_tca2	0.2	mol/mol	28	kab_cm	0.000094	1/day
2	fab_tdce_tca2	0.8	mol/mol	29	kan_teca2	0	1/day
3	fab_11dce_tca2	0.1	mol/mol	30	kan_tca2	0	1/day
4	fab_11dce_tca1	0.2	mol/mol	31	kan_dca2	0	1/day
5	fan_tca2_teca2	0	mol/mol	32	kan_ca	0	1/day
6	fan_cdce_teca2	0	mol/mol	33	kan_teca1	0	1/day
7	fan_tdce_teca2	0	mol/mol	34	kan_tca1	0	1/day
8	fan_dca2_tca2	0	mol/mol	35	kan_dca1	0	1/day
9	fan_vc_tca2	0	mol/mol	36	kan_pce	0	1/day
10	fan_ca_dca2	0	mol/mol	37	kan_tce	0	1/day
11	fan_tca1_teca1	0	mol/mol	38	kan_cdce	0	1/day
12	fan_11dce_teca1	0	mol/mol	39	kan_tdce	0	1/day
13	fan_cdce_tce	0	mol/mol	40	kan_11dce	0	1/day
14	fan_tdce_tce	0	mol/mol	41	kan_vc	0	1/day
15	fan_11dce_tce	0	mol/mol	42	kan_ct	0	1/day
16	fan_vc_cdce	0	mol/mol	43	kan_cf	0	1/day
17	fan_vc_tdce	0	mol/mol	44	kan_dcm	0	1/day
18	fan_vc_11dce	0	mol/mol	45	kan_cm	0	1/day
19	fan_cm_dcm	0	mol/mol	46	kae_dca2	0.005	1/day
20	kab_teca2	0.006	1/day	47	kae_ca	0.005	1/day
21	kab_tca2	0.0015	1/day	48	kae_cdce	0.005	1/day
22	kab_dca2	0.00003	1/day	49	kae_tdce	0.005	1/day
23	kab_ca	0.001	1/day	50	kae_11dce	0.005	1/day
24	kab_teca1	0.006	1/day	51	kae_vc	0.005	1/day
25	kab_tca1	0.001	1/day	52	kae_dcm	0.005	1/day
26	kab_dca1	0.00005	1/day	53	kae_cm	0.005	1/day
27	kab_ct	0.000047	1/day				

Table 10. Parameter Values For Example Simulation 3 – Anaerobic Case Equivalent to Table 20
– With The Mixed Chloroethene/Chloroethane/Chloromethane Dechlorination Reaction Module

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fab_cdce_tca2	0.2	mol/mol	28	kab_cm	0	1/day
2	fab_tdce_tca2	0.8	mol/mol	29	kan_teca2	0.005	1/day
3	fab_11dce_tca2	0	mol/mol	30	kan_tca2	0.01	1/day
4	fab_11dce_tca1	0	mol/mol	31	kan_dca2	0.025	1/day
5	fan_tca2_teca2	0	mol/mol	32	kan_ca	0.025	1/day
6	fan_cdce_teca2	0.2	mol/mol	33	kan_teca1	0	1/day
7	fan_tdce_teca2	0	mol/mol	34	kan_tca1	0	1/day
8	fan_dca2_tca2	0.2	mol/mol	35	kan_dca1	0	1/day
9	fan_vc_tca2	0.8	mol/mol	36	kan_pce	0.025	1/day
10	fan_ca_dca2	0.2	mol/mol	37	kan_tce	0.025	1/day
11	fan_tca1_teca1	0	mol/mol	38	kan_cdce	0.025	1/day
12	fan_11dce_teca1	0	mol/mol	39	kan_tdce	0.025	1/day
13	fan_cdce_tce	0.8	mol/mol	40	kan_11dce	0.025	1/day
14	fan_tdce_tce	0.2	mol/mol	41	kan_vc	0.0025	1/day
15	fan_11dce_tce	0	mol/mol	42	kan_ct	0	1/day
16	fan_vc_cdce	0.8	mol/mol	43	kan_cf	0	1/day
17	fan_vc_tdce	0.8	mol/mol	44	kan_dcm	0	1/day
18	fan_vc_11dce	0.8	mol/mol	45	kan_cm	0	1/day
19	fan_cm_dcm	0	mol/mol	46	kae_dca2	0	1/day
20	kab_teca2	0.006	1/day	47	kae_ca	0	1/day
21	kab_tca2	0	1/day	48	kae_cdce	0	1/day
22	kab_dca2	0.00003	1/day	49	kae_tdce	0	1/day
23	kab_ca	0.001	1/day	50	kae_11dce	0	1/day
24	kab_teca1	0	1/day	51	kae_vc	0	1/day
25	kab_tca1	0	1/day	52	kae_dcm	0	1/day
26	kab_dca1	0	1/day	53	kae_cm	0	1/day
27	kab_ct	0	1/day				

Table 11. Parameter Values for Example Simulation 4 – Aerobic Case Equivalent to Table 23 – with the Mixed Chloroethene/Chloroethane/Chloromethane Dechlorination Reaction Module

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fab_cdce_tca2	0.2	mol/mol	28	kab_cm	0	1/day
2	fab_tdce_tca2	0.8	mol/mol	29	kan_teca2	0	1/day
3	fab_11dce_tca2	0	mol/mol	30	kan_tca2	0	1/day
4	fab_11dce_tca1	0	mol/mol	31	kan_dca2	0	1/day
5	fan_tca2_teca2	0	mol/mol	32	kan_ca	0	1/day
6	fan_cdce_teca2	0	mol/mol	33	kan_teca1	0	1/day
7	fan_tdce_teca2	0	mol/mol	34	kan_tca1	0	1/day
8	fan_dca2_tca2	0	mol/mol	35	kan_dca1	0	1/day
9	fan_vc_tca2	0	mol/mol	36	kan_pce	0	1/day
10	fan_ca_dca2	0	mol/mol	37	kan_tce	0	1/day
11	fan_tca1_teca1	0	mol/mol	38	kan_cdce	0	1/day
12	fan_11dce_teca1	0	mol/mol	39	kan_tdce	0	1/day
13	fan_cdce_tce	0	mol/mol	40	kan_11dce	0	1/day
14	fan_tdce_tce	0	mol/mol	41	kan_vc	0	1/day
15	fan_11dce_tce	0	mol/mol	42	kan_ct	0	1/day
16	fan_vc_cdce	0	mol/mol	43	kan_cf	0	1/day
17	fan_vc_tdce	0	mol/mol	44	kan_dcm	0	1/day
18	fan_vc_11dce	0	mol/mol	45	kan_cm	0	1/day
19	fan_cm_dcm	0	mol/mol	46	kae_dca2	0.005	1/day
20	kab_teca2	0.006	1/day	47	kae_ca	0.005	1/day
21	kab_tca2	0	1/day	48	kae_cdce	0.005	1/day
22	kab_dca2	0.00003	1/day	49	kae_tdce	0.005	1/day
23	kab_ca	0.001	1/day	50	kae_11dce	0.005	1/day
24	kab_teca1	0	1/day	51	kae_vc	0.005	1/day
25	kab_tca1	0	1/day	52	kae_dcm	0.005	1/day
26	kab_dca1	0	1/day	53	kae_cm	0.005	1/day
27	kab_ct	0	1/day				

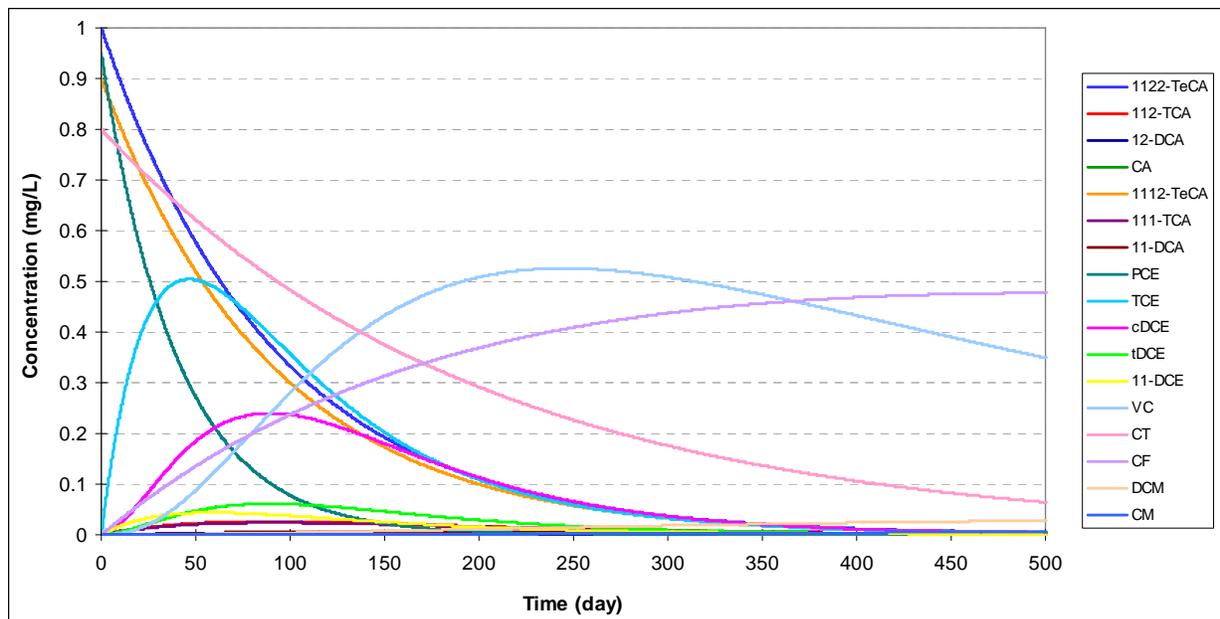


Figure 6. *Dechlorination of Mixed Chlorinated Solvents under Anaerobic Conditions Using the Parameter Values Shown in Table 8 — Initial concentrations were set to 1.0, 0.9, 0.95, and 0.8 mg/L for 1122TeCA, 1112TeCA, PCE, and CT, respectively. All other species concentrations started at zero.*

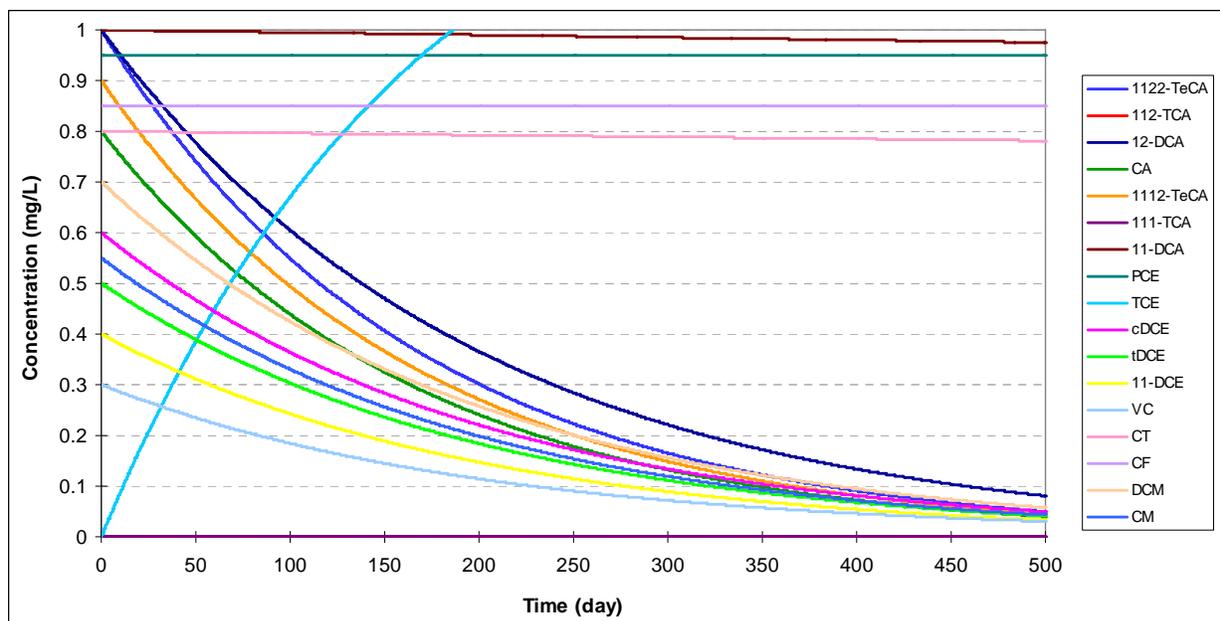


Figure 7. Dechlorination of Mixed Chlorinated Solvents under Aerobic Conditions Using the Parameter Values Shown in Table 9 — Initial concentrations were set to 1.0 mg/L for 1122TeCA, 12DCA, and 11DCA. Initial concentrations were set to 0.9, 0.95, 0.8, 0.8, 0.6, 0.5, 0.4, 0.3, 0.85, 0.7, and 0.55 mg/L for 1112TeCA, PCE, CT, CA, cDCE, tDCE, 11DCE, VC, CF, DCM, and CM, respectively. All other species concentrations started at zero.

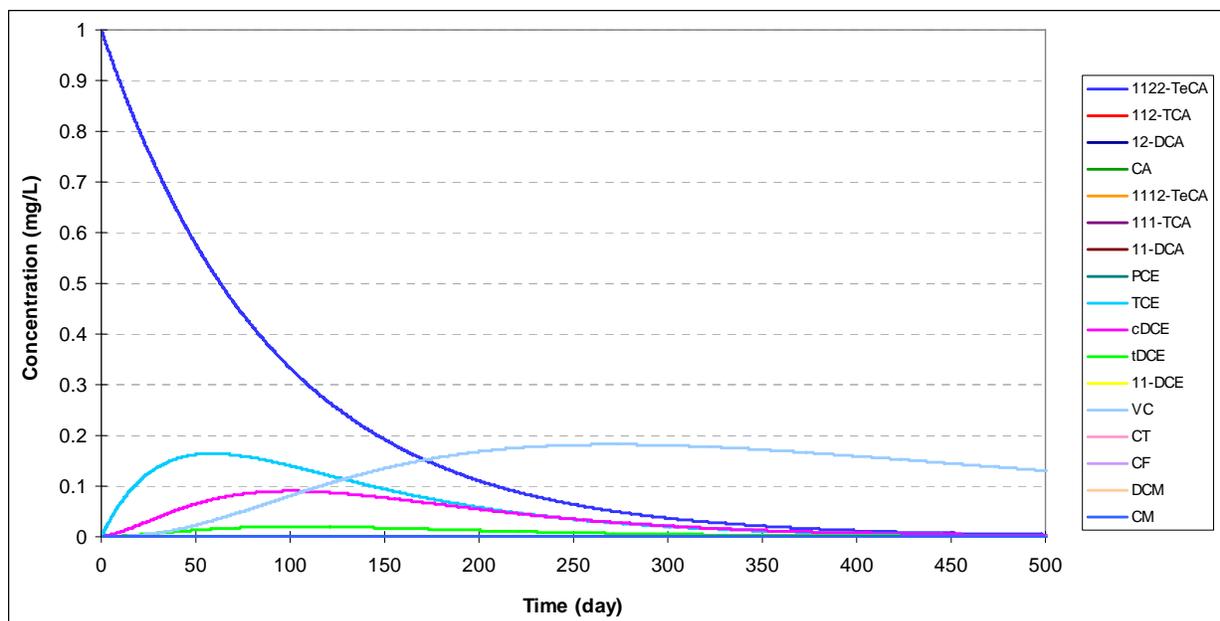


Figure 8. *Dechlorination of Mixed Chlorinated Solvents Using the Parameter Values Shown in Table 10 — The initial concentration of 1122TeCA was set to 1 mg/L. All other species concentrations started at zero. These results are the same as produced by the Dechlorination of 1,1,2,2-Tetrachloroethane and Chloroethenes reaction module (Figure 16).*

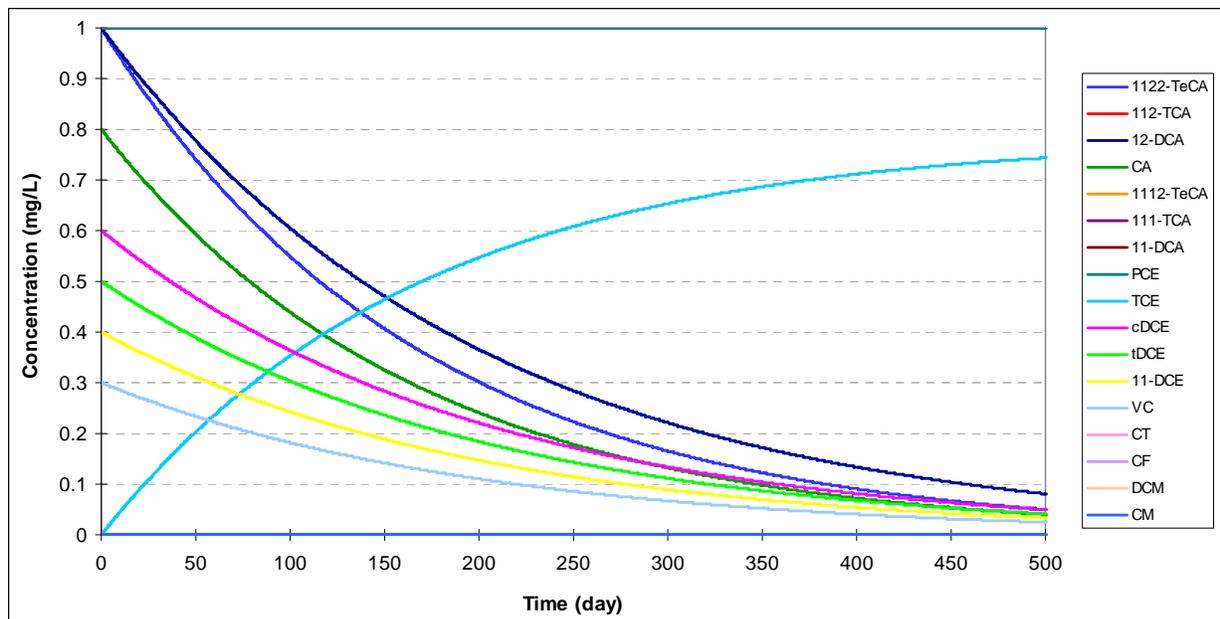


Figure 9. *Aerobic and Abiotic Degradation Using the Parameter Values Shown in Table 11 — The initial concentrations for 1122TeCA, 12DCA, and PCE were 1.0 mg/L. The initial concentrations were set to 0.8, 0.6, 0.5, 0.4, and 0.3 mg/L for CA, cDCE, tDCE, 11DCE, and VC, respectively. These results are the same as produced by the Dechlorination of 1,1,2,2-Tetrachloroethane and Chloroethenes reaction module (Figure 19).*

3.0 Chloromethane Dechlorination

3.1 Conceptual Model for Dechlorination Reactions

This reaction module describes dechlorination of carbon tetrachloride (tetrachloromethane) and related daughter products using first-order rate expressions. The module includes abiotic, aerobic, and anoxic/anaerobic reaction pathways, which the user may selectively turn off by setting the (spatially variable) values of the stoichiometric yields and/or the reaction rate constants to zero. See the section on RT3D MNA/EA Reaction Module Commonalities and the Discussion of Select Reaction Parameters for additional information on features common to all of these MNA/EA reaction modules and explanation of key reaction parameters.

Table 12 lists the chemical species included in this reaction module. Figure 10 shows the conceptual model describing the potential biotic and abiotic degradation pathways of chlorinated methane contaminants. See the conceptual model discussion for the Mixed Chloroethene/Chloroethane/Chloromethane Dechlorination reaction module for information on the development of the reaction pathways and the assumption of first-order reaction kinetics.

Table 12. Chemical Species Included in the Chloromethane Dechlorination Reaction Module

No.	Abbreviation ^a	Chemical Name	Selected Alternate Name	CAS ^b Registry Number	Molecular Weight ^c (g/mol)	Chemical Formula
1	CT	Tetrachloromethane	Carbon Tetrachloride	56-23-5	153.82270	CCl ₄
2	CF	Trichloromethane	Chloroform	67-66-3	119.37764	CHCl ₃
3	DCM	Dichloromethane	Methylene Dichloride, Methylene Chloride	75-09-2	84.93258	CH ₂ Cl ₂
4	CM	Chloromethane	Methyl Chloride	74-87-3	50.48752	CH ₃ Cl
5	Tracer	Conservative Tracer	—	N/A	N/A	N/A

^a These abbreviations refer to the specific chemicals listed here and should not be confused with different chemicals that may use the same abbreviation in other reaction modules.

^b CAS = Chemical Abstracts Service (see <http://www.cas.org/EO/regsys.html>)

^c Based on International Union of Pure and Applied Chemistry values reported by Loss [2003].

N/A – Not Applicable

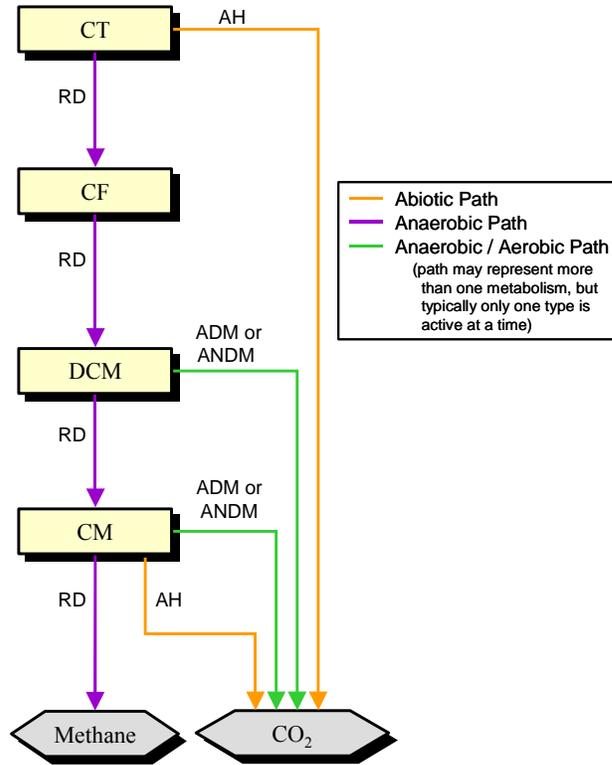


Figure 10. Conceptual Model for Dechlorination Reactions in the Chloromethane Dechlorination Reaction Module — Species in hexagonal shaded boxes are innocuous products and are not tracked in the reaction module. The reaction types for each pathway are described in Table 3.

3.2 Reaction Equations

The set of ODEs comprising this reaction module are shown in Equations 32 to 36. These ODEs describe the reaction kinetics for the 5 chemical species in Table 12. See Table 13 for a detailed itemization of all reaction parameters used in this reaction module.

$$\frac{dC_{CT}}{dt} = \left(-kan_{CT} \cdot C_{CT} - kab_{CT} \cdot C_{CT} \right) \quad (32)$$

$$\frac{dC_{CF}}{dt} = \left(Y_{CF} \cdot kan_{CT} \cdot C_{CT} - kan_{CF} \cdot C_{CF} \right) \quad (33)$$

$$\frac{dC_{DCM}}{dt} = \left(\begin{array}{l} Y_{DCM} \cdot kan_{CF} \cdot C_{CF} \\ - kan_{DCM} \cdot C_{DCM} - kae_{DCM} \cdot C_{DCM} \end{array} \right) \quad (34)$$

$$\frac{dC_{CM}}{dt} = \left(\begin{array}{l} \frac{Y_{CM}}{DCM} \cdot Fan_{\frac{CM}{DCM}} \cdot kan_{DCM} \cdot C_{DCM} \\ - kan_{CM} \cdot C_{CM} - kab_{CM} \cdot C_{CM} - kae_{CM} \cdot C_{CM} \end{array} \right) \quad (35)$$

$$\frac{dC_{Tracer}}{dt} = 0.0 \quad (\text{Conservative [non-reactive] tracer.}) \quad (36)$$

The first-order decay rate constants [T^{-1}] of the i^{th} species are represented in the equations above by the kan_i , kae_i , and kab_i terms for anaerobic biological reactions, aerobic biological reactions, or abiotic reactions, respectively. The concentration of the i^{th} species is represented by the C_i term [ML^{-3}]. The R_i terms represent the retardation factor for the i^{th} species [unitless].

In cases where multiple daughter products may be produced from dechlorination of a single parent species, the amount of each daughter species that is produced is a function of a mass yield [MM^{-1}] and a stoichiometric dechlorination yield [mol/mol]. The mass yield value, $Y_{d/p}$, accounts for the difference in molecular weight between the parent species "p" and the daughter species "d." All isomers of a daughter chemical have the same mass yield. Mass yield values are included in the reaction module code and do not need to be input by the user. The stoichiometric dechlorination yield represents the site-specific stoichiometry for each reaction pathway that occurs as either an anaerobic ($Fan_{d/p}$) or an abiotic process ($Fab_{d/p}$). The stoichiometric dechlorination yield is the fractional moles of daughter species that are produced by dechlorination of one mole of the parent species. The net yield is the product of the mass yield and the stoichiometric dechlorination yield. To preserve the mass balance, the values of the stoichiometric dechlorination yields are constrained by the relation in Equation 37.

$$Fan_{\frac{CM}{DCM}} \leq 1.0 \quad (37)$$

3.3 Required Input

The reaction parameters for this reaction module are made available to RT3D as part of the input for the Reaction Package. The Reaction Package input file structure is discussed in the RT3D manual and addendum [Clement, 1997; Clement and Johnson, 2002]. The 9 reaction parameters that must be specified for this reaction module are listed in Table 13 in the required order (ID Number) with units and a description. Site-specific knowledge from field data or laboratory tests should be applied to determine an appropriate model configuration for reaction parameters (i.e., the values and the spatial distribution).

Table 13. *Input Parameters for the Chloromethane Dechlorination Reaction Module*

ID #	Parameter	Fortran Variable	Units	Description
1	$Fan_{\frac{CM}{DCM}}$	fan_cm_dcm	mol/mol	Moles of CM produced from anaerobic decay of one mole of DCM
2	Kab_{CT}	kab_ct	1/day	First-order decay coefficient for abiotic dechlorination of CT
3	Kab_{CM}	kab_cm	1/day	First-order decay coefficient for abiotic dechlorination of CM
4	Kan_{CT}	kan_ct	1/day	First-order decay coefficient for anaerobic dechlorination of CT
5	Kan_{CF}	kan_cf	1/day	First-order decay coefficient for anaerobic dechlorination of CF
6	Kan_{DCM}	kan_dcm	1/day	First-order decay coefficient for anaerobic dechlorination of DCM
7	Kan_{CM}	kan_cm	1/day	First-order decay coefficient for anaerobic dechlorination of CM
8	Kae_{DCM}	kae_dcm	1/day	First-order decay coefficient for aerobic dechlorination of DCM
9	Kae_{CM}	kae_cm	1/day	First-order decay coefficient for aerobic dechlorination of CM

3.4 Example Simulations

Simulations with this reaction module were conducted with RT3D in a batch reactor (no flow) mode to show examples of how the reaction module simulates the pattern of dechlorination. The parameter values for each example simulation are listed in Tables 14 through 17. These parameters are arbitrary values and are not directly related to any specific laboratory data. Site-specific values would need to be determined as part of a calibration process. Results for these example batch simulations are shown in the Figures 11 through 14, respectively.

Table 14. *Parameter Values for Example Simulation 1 – Base Case Anaerobic Conditions – with the Chloromethane Dechlorination Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fan_cm_dcm	0.5	mol/mol	6	kan_dcm	0.005	1/day
2	kab_ct	0.000047	1/day	7	kan_cm	0.005	1/day
3	kab_cm	0.000094	1/day	8	kae_dcm	0	1/day
4	kan_ct	0.005	1/day	9	kae_cm	0	1/day
5	kan_cf	0.0005	1/day				

Table 15. *Parameter Values for Example Simulation 2 – Rates at 10% of Example Simulation 1 – with the Chloromethane Dechlorination Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fan_cm_dcm	0.5	mol/mol	6	kan_dcm	0.0005	1/day
2	kab_ct	0.0000047	1/day	7	kan_cm	0.0005	1/day
3	kab_cm	0.0000094	1/day	8	kae_dcm	0	1/day
4	kan_ct	0.0005	1/day	9	kae_cm	0	1/day
5	kan_cf	0.00005	1/day				

Table 16. Parameter Values for Example Simulation 3 – Different F Values Than Example Simulation 1 – with the Chloromethane Dechlorination Reaction Module

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fan_cm_dcm	0.1	mol/mol	6	kan_dcm	0.005	1/day
2	kab_ct	0.000047	1/day	7	kan_cm	0.005	1/day
3	kab_cm	0.000094	1/day	8	kae_dcm	0	1/day
4	kan_ct	0.005	1/day	9	kae_cm	0	1/day
5	kan_cf	0.0005	1/day				

Table 17. Parameter Values for Example Simulation 4 – Base Case Aerobic Conditions – with the Chloromethane Dechlorination Reaction Module

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fan_cm_dcm	0	mol/mol	6	kan_dcm	0	1/day
2	kab_ct	0.000047	1/day	7	kan_cm	0	1/day
3	kab_cm	0.000094	1/day	8	kae_dcm	0.005	1/day
4	kan_ct	0	1/day	9	kae_cm	0.005	1/day
5	kan_cf	0	1/day				

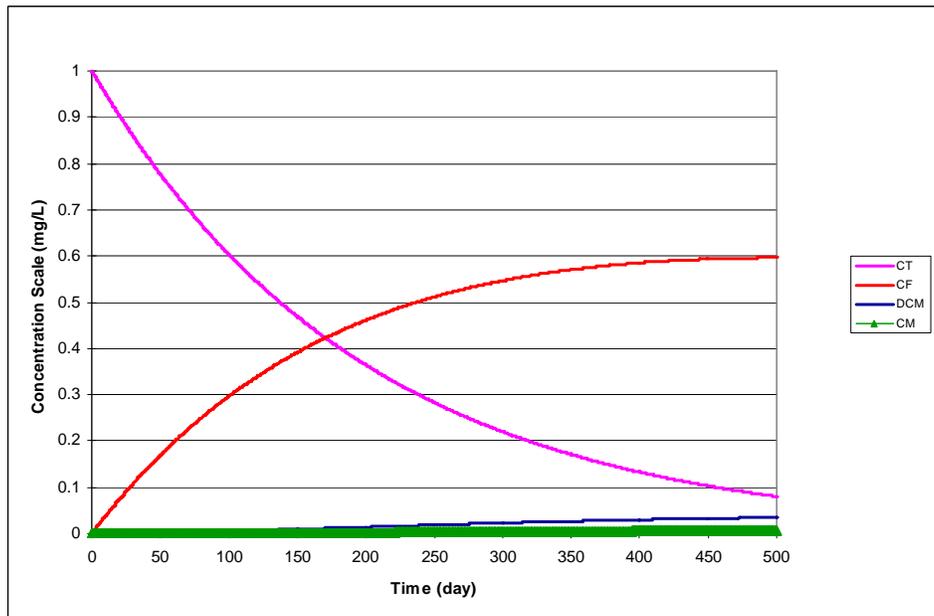


Figure 11. Dechlorination of CT Using the Parameter Values Shown in Table 14 — The initial concentration for CT was 1 mg/L. All other species concentrations started at zero.

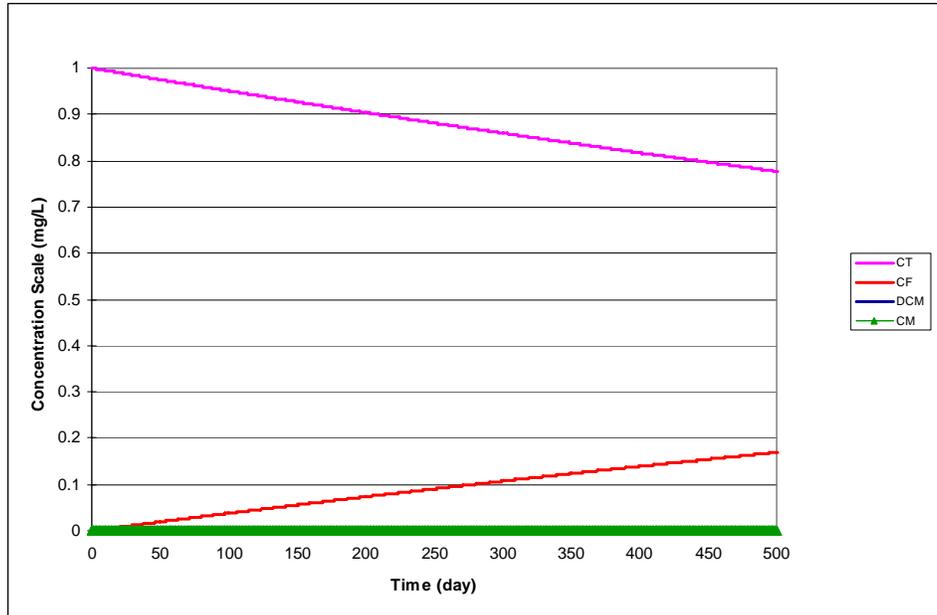


Figure 12. Dechlorination of CT Using the Parameter Values Shown in Table 15 — The initial concentration for CT was 1 mg/L. All other species concentrations started at zero.

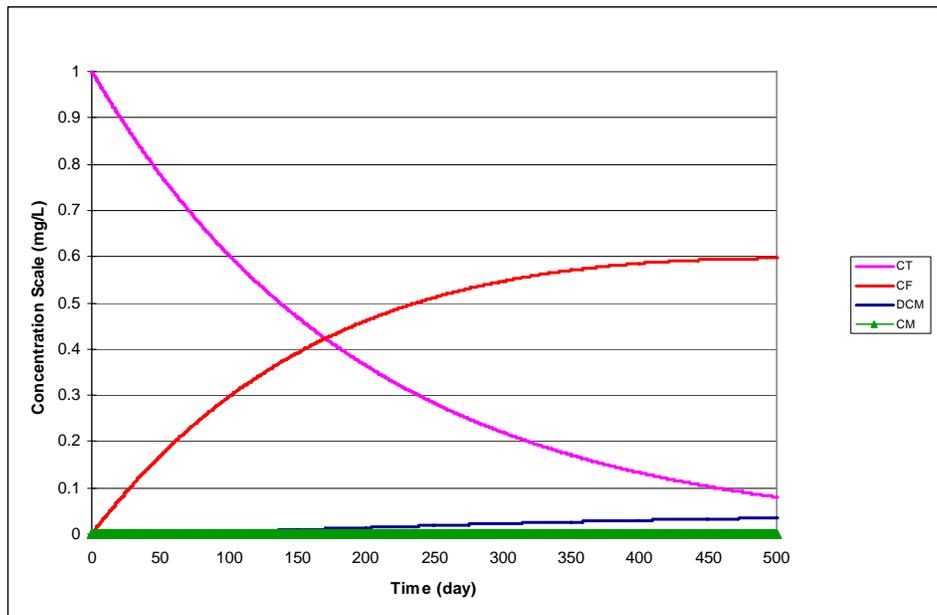


Figure 13. Dechlorination of CT Using the Parameter Values Shown in Table 16 — The initial concentration for CT was 1 mg/L. All other species concentrations started at zero.

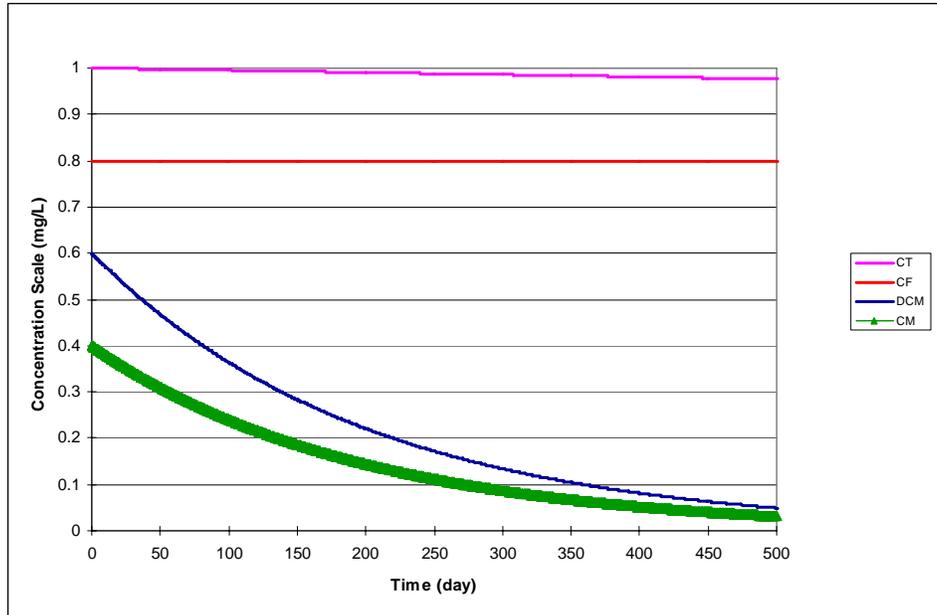


Figure 14. *Aerobic and Abiotic Degradation Using the Parameter Values Shown in Table 17 — The initial concentrations for CT, CF, DCM, and CM were 1, 0.8, 0.6, and 0.4 mg/L, respectively.*

4.0 Dechlorination of 1,1,2,2-Tetrachloroethane and Chloroethenes

4.1 Conceptual Model for Dechlorination Reactions

This reaction module describes dechlorination of 1,1,2,2-tetrachloroethane, tetrachloroethene, and related daughter products (including 1,1,2-TCA and 1,2-DCA) using first-order rate expressions. The module includes abiotic, aerobic, and anoxic/anaerobic reaction pathways, which the user may selectively turn off by setting the (spatially variable) values of the stoichiometric yields and/or the reaction rate constants to zero. See the section on RT3D MNA/EA Reaction Module Commonalities and the Discussion of Select Reaction Parameters for additional information on features common to all of these MNA/EA reaction modules and explanation of key reaction parameters.

Table 18 lists the chemical species included in this reaction module. Dechlorination reactions for chlorinated ethane contaminants can result in formation of chlorinated ethene species, so this reaction module combines the reaction pathways for these two groups of contaminants. Figure 15 shows the conceptual model describing the potential biotic and abiotic degradation pathways of both chlorinated ethene and chlorinated ethane contaminants. See the conceptual model discussion for the Mixed Chloroethene/ Chloroethane/Chloromethane Dechlorination reaction module for information on the development of the reaction pathways and the assumption of first-order reaction kinetics.

Table 18. Chemical Species Included in the Dechlorination of 1,1,2,2-Tetrachloroethane and Chloroethenes Reaction Module

No.	Abbreviation ^a	Chemical Name	Selected Alternate Name	CAS ^b Registry Number	Molecular Weight ^c (g/mol)	Chemical Formula
1	TeCA	1,1,2,2-Tetrachloroethane	1,1,2,2-TeCA	79-34-5	167.84928	C ₂ H ₂ Cl ₄
2	TCA	1,1,2-Trichloroethane	Vinyl Trichloride; 1,1,2-TCA	79-00-5	133.40422	C ₂ H ₃ Cl ₃
3	DCA	1,2-Dichloroethane	Ethane Dichloride; 1,2-DCA	107-06-2	98.95916	C ₂ H ₄ Cl ₂
4	CA	Chloroethane	Ethyl Chloride	75-00-3	64.5141	C ₂ H ₅ Cl
5	PCE	Tetrachloroethene	Tetrachloroethylene; Perchloroethylene	127-18-4	165.8334	C ₂ Cl ₄
6	TCE	Trichloroethene	Trichloroethylene	79-01-6	131.38834	C ₂ HCl ₃
7	cDCE	cis-1,2-Dichloroethene	cis-1,2-Dichloroethylene; cis-1,2-DCE; cis-DCE	156-59-2	96.94328	C ₂ H ₂ Cl ₂
8	tDCE	trans-1,2-Dichloroethene	trans-1,2-Dichloroethylene; trans-1,2-DCE; trans-DCE	156-60-5	96.94328	C ₂ H ₂ Cl ₂
9	11DCE	1,1-Dichloroethene	Vinylidene Chloride; 1,1-DCE	75-35-4	96.94328	C ₂ H ₂ Cl ₂
10	VC	Chloroethene	Vinyl Chloride	75-01-4	62.49822	C ₂ H ₃ Cl
11	Tracer	Conservative Tracer	—	N/A	N/A	N/A

^a These abbreviations refer to the specific chemicals listed here and should not be confused with different chemicals that may use the same abbreviation in other reaction modules.

^b CAS = Chemical Abstracts Service (see <http://www.cas.org/EO/regsys.html>)

^c Based on International Union of Pure and Applied Chemistry values reported by Loss [2003].

N/A – Not Applicable

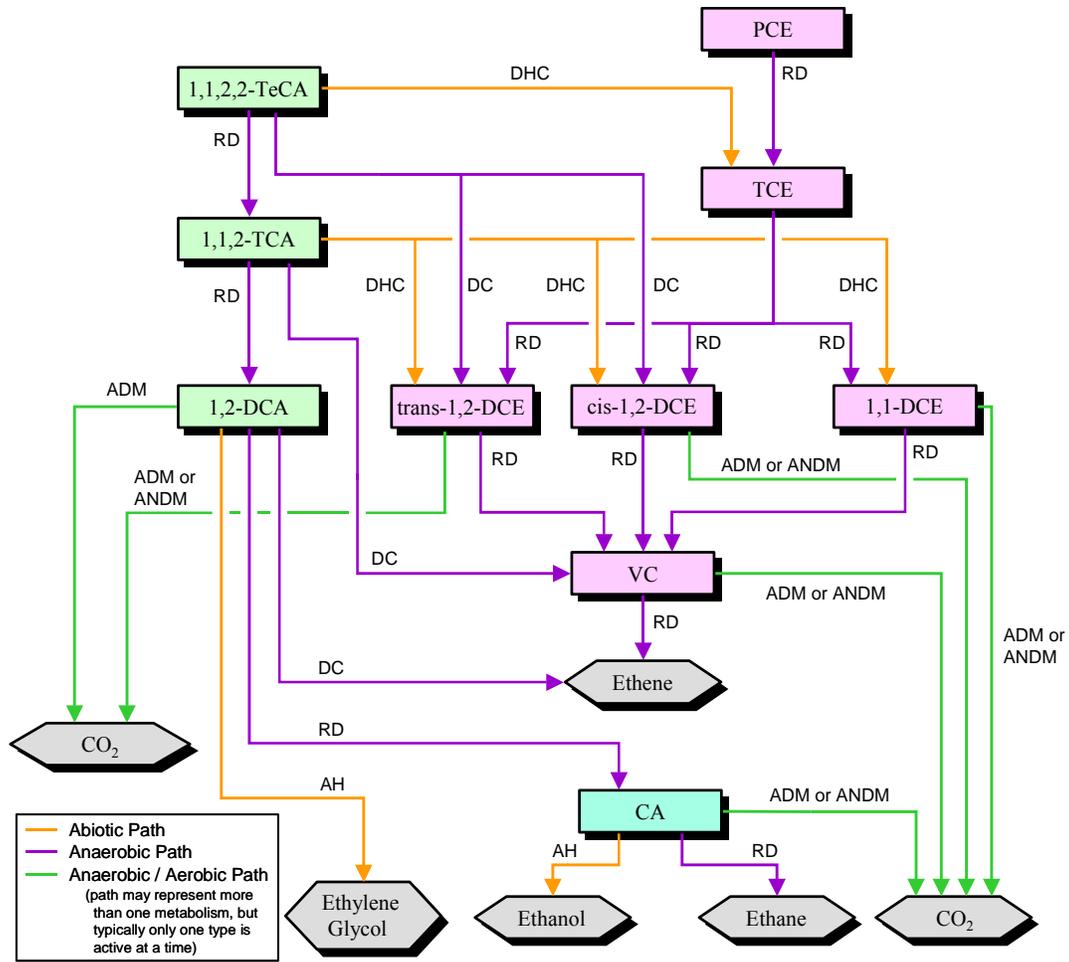


Figure 15. Conceptual Model for Dechlorination Reactions in the Dechlorination of 1,1,2,2-Tetrachloroethane and Chloroethenes Reaction Module — Species in hexagonal shaded boxes are innocuous products and are not tracked in the reaction module. The reaction types for each pathway are described in Table 3.

4.2 Reaction Equations

The set of ODEs comprising this reaction module are shown in Equations 38 to 48. These ODEs describe the reaction kinetics for the 11 chemical species in Table 18. See Table 19 for a detailed itemization of all reaction parameters used in this reaction module.

$$\frac{dC_{TeCA}}{dt} = \left(-kan_{TeCA} \cdot C_{TeCA} - kab_{TeCA} \cdot C_{TeCA} \right) \quad (38)$$

$$\frac{dC_{TCA}}{dt} = \left(Y_{TCA} \cdot Fan_{TCA} \cdot kan_{TeCA} \cdot C_{TeCA} - kan_{TCA} \cdot C_{TCA} - kab_{TCA} \cdot C_{TCA} \right) \quad (39)$$

$$\frac{dC_{DCA}}{dt} = \left(\begin{array}{l} \frac{Y_{DCA}}{TCA} \cdot Fan_{DCA} \cdot kan_{TCA} \cdot C_{TCA} \\ - kan_{DCA} \cdot C_{DCA} - kab_{DCA} \cdot C_{DCA} - kae_{DCA} \cdot C_{DCA} \end{array} \right) \quad (40)$$

$$\frac{dC_{CA}}{dt} = \left(\begin{array}{l} \frac{Y_{CA}}{DCA} \cdot Fan_{CA} \cdot kan_{DCA} \cdot C_{DCA} \\ - kan_{CA} \cdot C_{CA} - kab_{CA} \cdot C_{CA} - kae_{CA} \cdot C_{CA} \end{array} \right) \quad (41)$$

$$\frac{dC_{PCE}}{dt} = \left(- kan_{PCE} \cdot C_{PCE} \right) \quad (42)$$

$$\frac{dC_{TCE}}{dt} = \left(\begin{array}{l} Y_{TCE} \cdot kan_{PCE} \cdot C_{PCE} + Y_{TCE} \cdot kab_{TeCA} \cdot C_{TeCA} - kan_{TCE} \cdot C_{TCE} \end{array} \right) \quad (43)$$

$$\frac{dC_{cDCE}}{dt} = \left(\begin{array}{l} \frac{Y_{DCE}}{TeCA} \cdot Fan_{cDCE} \cdot kan_{TeCA} \cdot C_{TeCA} + \frac{Y_{DCE}}{TCE} \cdot Fan_{cDCE} \cdot kan_{TCE} \cdot C_{TCE} \\ + Y_{DCE} \cdot Fab_{cDCE} \cdot kab_{TCA} \cdot C_{TCA} \\ - kan_{cDCE} \cdot C_{cDCE} - kae_{cDCE} \cdot C_{cDCE} \end{array} \right) \quad (44)$$

$$\frac{dC_{iDCE}}{dt} = \left(\begin{array}{l} \frac{Y_{DCE}}{TeCA} \cdot Fan_{iDCE} \cdot kan_{TeCA} \cdot C_{TeCA} + \frac{Y_{DCE}}{TCE} \cdot Fan_{iDCE} \cdot kan_{TCE} \cdot C_{TCE} \\ + Y_{DCE} \cdot Fab_{iDCE} \cdot kab_{TCA} \cdot C_{TCA} \\ - kan_{iDCE} \cdot C_{iDCE} - kae_{iDCE} \cdot C_{iDCE} \end{array} \right) \quad (45)$$

$$\frac{dC_{11DCE}}{dt} = \left(\begin{array}{l} \frac{Y_{DCE}}{TCE} \cdot Fan_{11DCE} \cdot kan_{TCE} \cdot C_{TCE} + \frac{Y_{DCE}}{TCA} \cdot Fab_{11DCE} \cdot kab_{TCA} \cdot C_{TCA} \\ - kan_{11DCE} \cdot C_{11DCE} - kae_{11DCE} \cdot C_{11DCE} \end{array} \right) \quad (46)$$

$$\frac{dC_{VC}}{dt} = \left(\begin{array}{l} \frac{Y_{VC}}{TCA} \cdot \frac{Fan_{VC}}{TCA} \cdot kan_{TCA} \cdot C_{TCA} + \frac{Y_{VC}}{DCE} \cdot \frac{Fan_{VC}}{cDCE} \cdot kan_{cDCE} \cdot C_{cDCE} \\ + \frac{Y_{VC}}{DCE} \cdot \frac{Fan_{VC}}{iDCE} \cdot kan_{iDCE} \cdot C_{iDCE} \\ + \frac{Y_{VC}}{DCE} \cdot \frac{Fan_{VC}}{11DCE} \cdot kan_{11DCE} \cdot C_{11DCE} \\ - kan_{VC} \cdot C_{VC} - kae_{VC} \cdot C_{VC} \end{array} \right) \quad (47)$$

$$\frac{dC_{Tracer}}{dt} = 0.0 \quad (\text{Conservative [non-reactive] tracer.}) \quad (48)$$

The first-order decay rate constants [T^{-1}] of the i^{th} species are represented in the equations above by the kan_i , kae_i , and kab_i terms for anaerobic biological reactions, aerobic biological reactions, or abiotic reactions, respectively. The concentration of the i^{th} species is represented by the C_i term [ML^{-3}]. The R_i terms represent the retardation factor for the i^{th} species [unitless].

In cases where multiple daughter products may be produced from dechlorination of a single parent species, the amount of each daughter species that is produced is a function of a mass yield [MM^{-1}] and a stoichiometric dechlorination yield [mol/mol]. The mass yield value, $Y_{d/p}$, accounts for the difference in molecular weight between the parent species "p" and the daughter species "d." All isomers of a daughter chemical have the same mass yield. Mass yield values are included in the reaction module code and do not need to be input by the user. The stoichiometric dechlorination yield represents the site-specific stoichiometry for each reaction pathway that occurs as either an anaerobic ($Fan_{d/p}$) or an abiotic process ($Fab_{d/p}$). The stoichiometric dechlorination yield is the fractional moles of daughter species that are produced by dechlorination of one mole of the parent species. The net yield is the product of the mass yield and the stoichiometric dechlorination yield. To preserve the mass balance, the values of the stoichiometric dechlorination yields are constrained by the relations in Equations 49 to 56.

$$\frac{Fan_{TCA}}{TeCA} + \frac{Fan_{cDCE}}{TeCA} + \frac{Fan_{iDCE}}{TeCA} = 1.0 \quad (49)$$

$$\frac{Fan_{DCA}}{TCA} + \frac{Fan_{VC}}{TCA} = 1.0 \quad (50)$$

$$\frac{Fan_{cDCE}}{TCE} + \frac{Fan_{iDCE}}{TCE} + \frac{Fan_{11DCE}}{TCE} = 1.0 \quad (51)$$

$$\frac{Fab_{cDCE}}{TCA} + \frac{Fab_{iDCE}}{TCA} + \frac{Fab_{11DCE}}{TCA} = 1.0 \quad (52)$$

$$Fan_{\frac{CA}{DCA}} \leq 1.0 \quad (53)$$

$$Fan_{\frac{VC}{cDCE}} \leq 1.0 \quad (54)$$

$$Fan_{\frac{VC}{iDCE}} \leq 1.0 \quad (55)$$

$$Fan_{\frac{VC}{11DCE}} \leq 1.0 \quad (56)$$

4.3 Required Input

The reaction parameters for this reaction module are made available to RT3D as part of the input for the Reaction Package. The Reaction Package input file structure is discussed in the RT3D manual and addendum [Clement, 1997; Clement and Johnson, 2002]. The 35 reaction parameters that must be specified for this reaction module are listed in Table 19 in the required order (ID Number) with units and a description. Site-specific knowledge from field data or laboratory tests should be applied to determine an appropriate model configuration for reaction parameters (i.e., the values and the spatial distribution).

Table 19. Input Parameters for the Dechlorination of 1,1,2,2-Tetrachloroethane and Chloroethenes Reaction Module

ID #	Parameter	Fortran Variable	Units	Description
1	$Fab_{\frac{cDCE}{TCA}}$	fab_cdce_tca	mol/mol	Moles of cis-1,2-DCE produced from abiotic decay of one mole of TCA
2	$Fab_{\frac{iDCE}{TCA}}$	fab_tdce_tca	mol/mol	Moles of trans-1,2-DCE produced from abiotic decay of one mole of TCA
3	$Fab_{\frac{11DCE}{TCA}}$	fab_11dce_tca	mol/mol	Moles of 1,1-DCE produced from abiotic decay of one mole of TCA
4	$Fan_{\frac{TCA}{TeCA}}$	fan_tca_teca	mol/mol	Moles of TCA produced from anaerobic decay of one mole of TeCA
5	$Fan_{\frac{cDCE}{TeCA}}$	fan_cdce_teca	mol/mol	Moles of cis-1,2-DCE produced from anaerobic decay of one mole of TeCA
6	$Fan_{\frac{iDCE}{TeCA}}$	fan_tdce_teca	mol/mol	Moles of trans-1,2-DCE produced from anaerobic decay of one mole of TeCA
7	$Fan_{\frac{DCA}{TCA}}$	fan_dca_tca	mol/mol	Moles of DCA produced from anaerobic decay of one mole of TCA

Table 19. (contd)

ID #	Parameter	Fortran Variable	Units	Description
8	$Fan_{\frac{VC}{TCA}}$	fan_vc_tca	mol/mol	Moles of VC produced from anaerobic decay of one mole of TCA
9	$Fan_{\frac{CA}{DCA}}$	fan_ca_dca	mol/mol	Moles of CA produced from anaerobic decay of one mole of DCA
10	$Fan_{\frac{cDCE}{TCE}}$	fan_cdce_tce	mol/mol	Moles of cis-1,2-DCE produced from anaerobic decay of one mole of TCE
11	$Fan_{\frac{iDCE}{TCE}}$	fan_tdce_tce	mol/mol	Moles of trans-1,2-DCE produced from anaerobic decay of one mole of TCE
12	$Fan_{\frac{11DCE}{TCE}}$	fan_11dce_tce	mol/mol	Moles of 1,1-DCE produced from anaerobic decay of one mole of TCE
13	$Fan_{\frac{VC}{cDCE}}$	fan_vc_cdce	mol/mol	Moles of VC produced from anaerobic decay of one mole of cis-1,2-DCE
14	$Fan_{\frac{VC}{iDCE}}$	fan_vc_tdce	mol/mol	Moles of VC produced from anaerobic decay of one mole of trans-1,2-DCE
15	$Fan_{\frac{VC}{11DCE}}$	fan_vc_11dce	mol/mol	Moles of VC produced from anaerobic decay of one mole of 1,1-DCE
16	kab_{TeCA}	kab_teca	1/day	First-order decay coefficient for abiotic dechlorination of TeCA
17	kab_{TCA}	kab_tca	1/day	First-order decay coefficient for abiotic dechlorination of TCA
18	kab_{DCA}	kab_dca	1/day	First-order decay coefficient for abiotic dechlorination of DCA
19	kab_{CA}	kab_ca	1/day	First-order decay coefficient for abiotic dechlorination of CA
20	kan_{TeCA}	kan_teca	1/day	First-order decay coefficient for anaerobic dechlorination of TeCA
21	kan_{TCA}	kan_tca	1/day	First-order decay coefficient for anaerobic dechlorination of TCA
22	kan_{DCA}	kan_dca	1/day	First-order decay coefficient for anaerobic dechlorination of DCA
23	kan_{CA}	kan_ca	1/day	First-order decay coefficient for anaerobic dechlorination of CA
24	kan_{PCE}	kan_pce	1/day	First-order decay coefficient for anaerobic dechlorination of PCE
25	kan_{TCE}	kan_tce	1/day	First-order decay coefficient for anaerobic dechlorination of TCE
26	kan_{cDCE}	kan_cdce	1/day	First-order decay coefficient for anaerobic dechlorination of cis-1,2-DCE
27	kan_{iDCE}	kan_tdce	1/day	First-order decay coefficient for anaerobic dechlorination of trans-1,2-DCE

Table 19. (contd)

ID #	Parameter	Fortran Variable	Units	Description
28	kan_{11DCE}	kan_11dce	1/day	First-order decay coefficient for anaerobic dechlorination of 1,1-DCE
29	kan_{VC}	kan_vc	1/day	First-order decay coefficient for anaerobic dechlorination of VC
30	kae_{DCA}	kae_dca	1/day	First-order decay coefficient for aerobic dechlorination of DCA
31	kae_{CA}	kae_ca	1/day	First-order decay coefficient for aerobic dechlorination of CA
32	kae_{cDCE}	kae_cdce	1/day	First-order decay coefficient for aerobic dechlorination of cis-1,2-DCE
33	kae_{tDCE}	kae_tdce	1/day	First-order decay coefficient for aerobic dechlorination of trans-1,2-DCE
34	kae_{11DCE}	kae_11dce	1/day	First-order decay coefficient for aerobic dechlorination of 1,1-DCE
35	kae_{VC}	kae_vc	1/day	First-order decay coefficient for aerobic dechlorination of VC

4.4 Example Simulations

Simulations with this reaction module were conducted with RT3D in a batch reactor (no flow) mode to show examples of how the reaction module simulates the pattern of dechlorination. The parameter values for each example simulation are listed in Tables 20 through 23. These parameters are arbitrary values and are not directly related to any specific laboratory data. Site-specific values would need to be determined as part of a calibration process. Results for these example batch simulations are shown in the Figures 16 through 19, respectively.

Table 20. Parameter Values for Example Simulation 1 – Base Case Anaerobic Conditions – with the Dechlorination of 1,1,2,2-Tetrachloroethane and Chloroethenes Reaction Module

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fab_cdce_tca	0.2	mol/mol	19	kab_ca	0.001	1/day
2	fab_tdce_tca	0.8	mol/mol	20	kan_teca	0.005	1/day
3	fab_11dce_tca	0	mol/mol	21	kan_tca	0.01	1/day
4	fan_tca_teca	0	mol/mol	22	kan_dca	0.025	1/day
5	fan_cdce_teca	0.2	mol/mol	23	kan_ca	0.025	1/day
6	fan_tdce_teca	0	mol/mol	24	kan_pce	0.025	1/day
7	fan_dca_tca	0.2	mol/mol	25	kan_tce	0.025	1/day
8	fan_vc_tca	0.8	mol/mol	26	kan_cdce	0.025	1/day
9	fan_ca_dca	0.2	mol/mol	27	kan_tdce	0.025	1/day
10	fan_cdce_tce	0.8	mol/mol	28	kan_11dce	0.025	1/day
11	fan_tdce_tce	0.2	mol/mol	29	kan_vc	0.0025	1/day
12	fan_11dce_tce	0	mol/mol	30	kae_dca	0	1/day
13	fan_vc_cdce	0.8	mol/mol	31	kae_ca	0	1/day
14	fan_vc_tdce	0.8	mol/mol	32	kae_cdce	0	1/day
15	fan_vc_11dce	0.8	mol/mol	33	kae_tdce	0	1/day
16	kab_teca	0.006	1/day	34	kae_11dce	0	1/day
17	kab_tca	0	1/day	35	kae_vc	0	1/day
18	kab_dca	0.00003	1/day				

Table 21. Parameter Values for Example Simulation 2 – Rates at 10% of Example Simulation 1 – with the Dechlorination of 1,1,2,2-Tetrachloroethane and Chloroethenes Reaction Module

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fab_cdce_tca	0.2	mol/mol	19	kab_ca	0.0001	1/day
2	fab_tdce_tca	0.8	mol/mol	20	kan_teca	0.0005	1/day
3	fab_11dce_tca	0	mol/mol	21	kan_tca	0.001	1/day
4	fan_tca_teca	0	mol/mol	22	kan_dca	0.0025	1/day
5	fan_cdce_teca	0.2	mol/mol	23	kan_ca	0.0025	1/day
6	fan_tdce_teca	0	mol/mol	24	kan_pce	0.0025	1/day
7	fan_dca_tca	0.2	mol/mol	25	kan_tce	0.0025	1/day
8	fan_vc_tca	0.8	mol/mol	26	kan_cdce	0.0025	1/day
9	fan_ca_dca	0.2	mol/mol	27	kan_tdce	0.0025	1/day
10	fan_cdce_tce	0.8	mol/mol	28	kan_11dce	0.0025	1/day
11	fan_tdce_tce	0.2	mol/mol	29	kan_vc	0.00025	1/day
12	fan_11dce_tce	0	mol/mol	30	kae_dca	0	1/day
13	fan_vc_cdce	0.8	mol/mol	31	kae_ca	0	1/day
14	fan_vc_tdce	0.8	mol/mol	32	kae_cdce	0	1/day
15	fan_vc_11dce	0.8	mol/mol	33	kae_tdce	0	1/day
16	kab_teca	0.0006	1/day	34	kae_11dce	0	1/day
17	kab_tca	0	1/day	35	kae_vc	0	1/day
18	kab_dca	0.000003	1/day				

Table 22. Parameter Values for Example Simulation 3 – Different F Values Than Example Simulation 1 – with the Dechlorination of 1,1,2,2-Tetrachloroethane and Chloroethenes Reaction Module.

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fab_cdce_tca	0.2	mol/mol	19	kab_ca	0.001	1/day
2	fab_tdce_tca	0.8	mol/mol	20	kan_teca	0.005	1/day
3	fab_11dce_tca	0	mol/mol	21	kan_tca	0.01	1/day
4	fan_tca_teca	0.8	mol/mol	22	kan_dca	0.025	1/day
5	fan_cdce_teca	0	mol/mol	23	kan_ca	0.025	1/day
6	fan_tdce_teca	0.2	mol/mol	24	kan_pce	0.025	1/day
7	fan_dca_tca	0.8	mol/mol	25	kan_tce	0.025	1/day
8	fan_vc_tca	0.2	mol/mol	26	kan_cdce	0.025	1/day
9	fan_ca_dca	0.8	mol/mol	27	kan_tdce	0.025	1/day
10	fan_cdce_tce	0.2	mol/mol	28	kan_11dce	0.025	1/day
11	fan_tdce_tce	0	mol/mol	29	kan_vc	0.0025	1/day
12	fan_11dce_tce	0.8	mol/mol	30	kae_dca	0	1/day
13	fan_vc_cdce	0.2	mol/mol	31	kae_ca	0	1/day
14	fan_vc_tdce	0.2	mol/mol	32	kae_cdce	0	1/day
15	fan_vc_11dce	0.2	mol/mol	33	kae_tdce	0	1/day
16	kab_teca	0.006	1/day	34	kae_11dce	0	1/day
17	kab_tca	0	1/day	35	kae_vc	0	1/day
18	kab_dca	0.00003	1/day				

Table 23. Parameter Values for Example Simulation 4 – Base Case Aerobic Conditions – with the Dechlorination of 1,1,2,2-Tetrachloroethane and Chloroethenes Reaction Module

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fab_cdce_tca	0.2	mol/mol	19	kab_ca	0.001	1/day
2	fab_tdce_tca	0.8	mol/mol	20	kan_teca	0	1/day
3	fab_11dce_tca	0	mol/mol	21	kan_tca	0	1/day
4	fan_tca_teca	0	mol/mol	22	kan_dca	0	1/day
5	fan_cdce_teca	0	mol/mol	23	kan_ca	0	1/day
6	fan_tdce_teca	0	mol/mol	24	kan_pce	0	1/day
7	fan_dca_tca	0	mol/mol	25	kan_tce	0	1/day
8	fan_vc_tca	0	mol/mol	26	kan_cdce	0	1/day
9	fan_ca_dca	0	mol/mol	27	kan_tdce	0	1/day
10	fan_cdce_tce	0	mol/mol	28	kan_11dce	0	1/day
11	fan_tdce_tce	0	mol/mol	29	kan_vc	0	1/day
12	fan_11dce_tce	0	mol/mol	30	kae_dca	0.005	1/day
13	fan_vc_cdce	0	mol/mol	31	kae_ca	0.005	1/day
14	fan_vc_tdce	0	mol/mol	32	kae_cdce	0.005	1/day
15	fan_vc_11dce	0	mol/mol	33	kae_tdce	0.005	1/day
16	kab_teca	0.006	1/day	34	kae_11dce	0.005	1/day
17	kab_tca	0	1/day	35	kae_vc	0.005	1/day
18	kab_dca	0.00003	1/day				

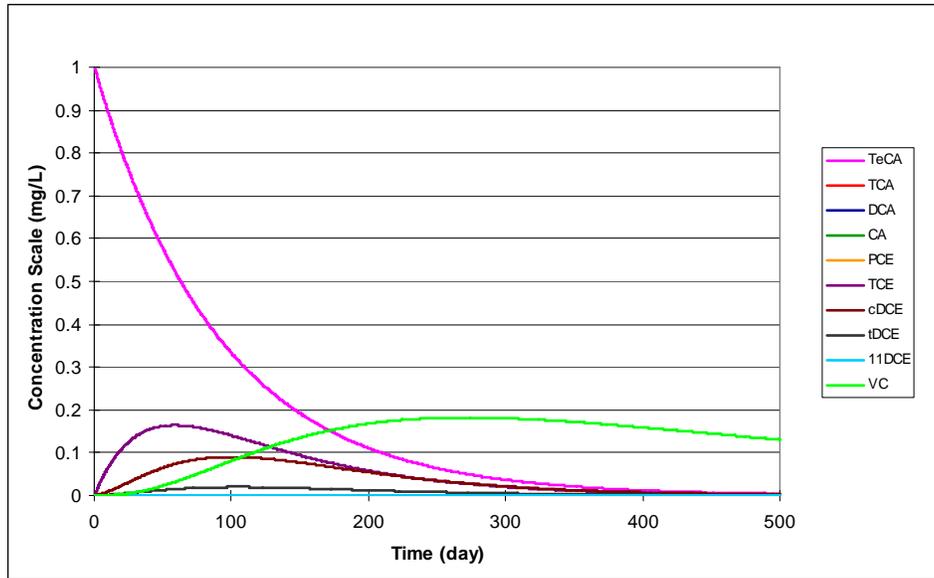


Figure 16. Dechlorination of 1,1,2,2-TeCA Using the Parameter Values Shown in Table 20 — The initial concentration for TeCA was 1 mg/L. All other species concentrations started at zero. In the results, the concentrations of TCA, DCA, CA, PCE, and 11DCE are zero.

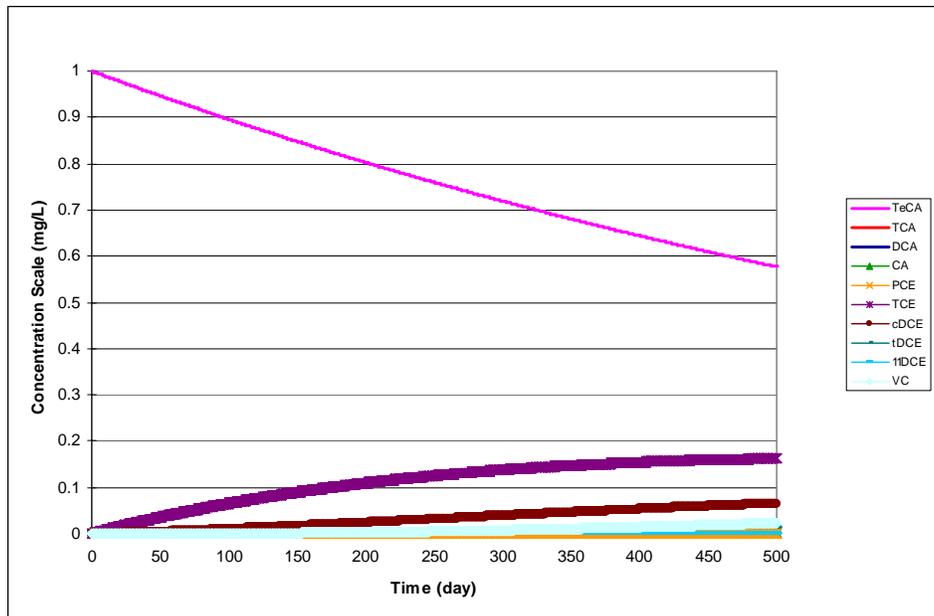


Figure 17. Dechlorination of 1,1,2,2-TeCA Using the Parameter Values Shown in Table 21 — The initial concentration for TeCA was 1 mg/L. All other species concentrations started at zero.

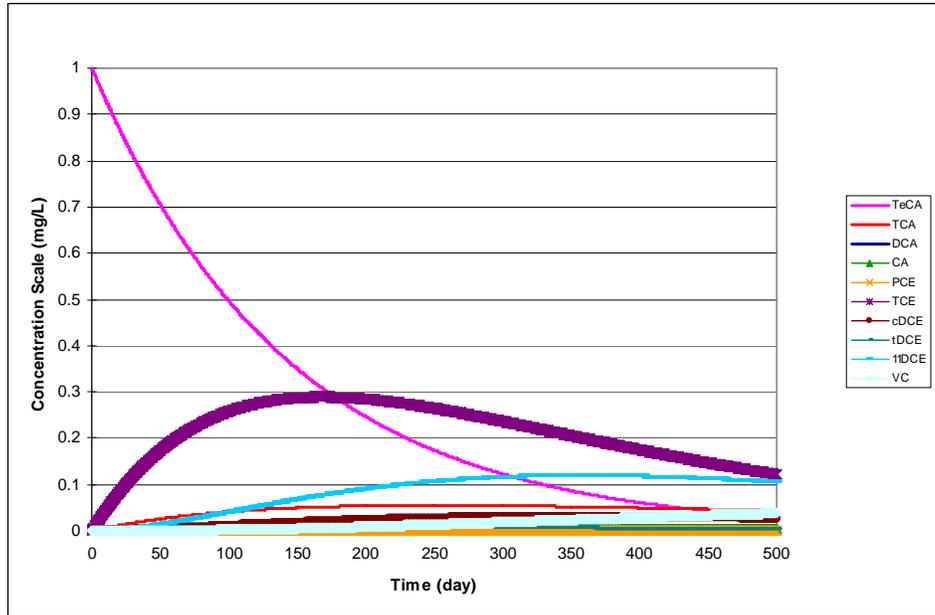


Figure 18. Dechlorination of 1,1,2,2-TeCA Using the Parameter Values Shown in Table 22 — The initial concentration for TeCA was 1 mg/L. All other species concentrations started at zero.

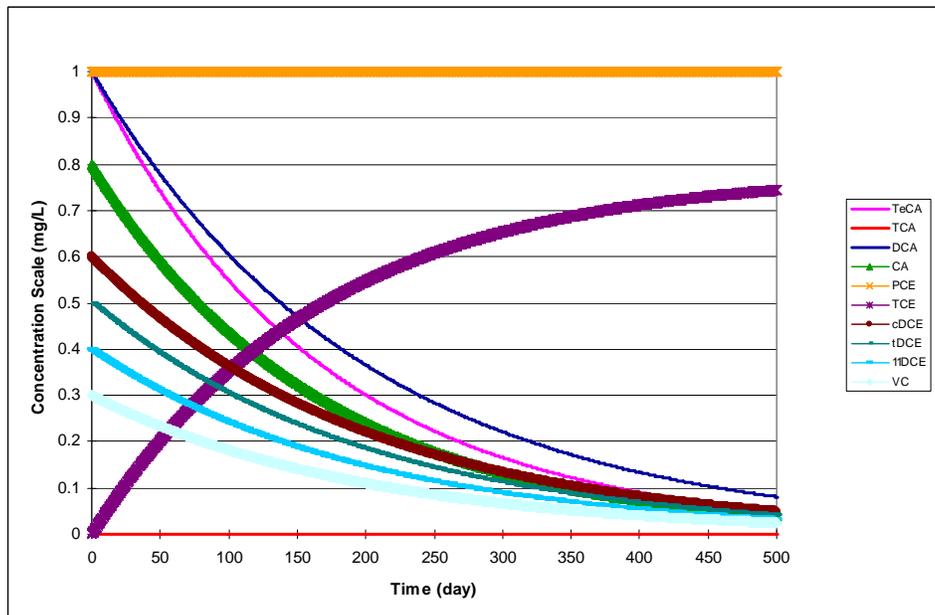


Figure 19. Aerobic and Abiotic Degradation of Contaminants in the 1,1,2,2-TeCA and PCE Families Using the Parameter Values Shown in Table 23 — The initial concentrations for TeCA, TCA, DCA, CA, PCE, TCE, cDCE, tDCE, 11DCE, and VC were 1, 0, 1, 0.8, 1, 0, 0.6, 0.5, 0.4, and 0.3 mg/L, respectively.

5.0 Dechlorination of 1,1,1,2-Tetrachloroethane and Chloroethenes

5.1 Conceptual Model for Dechlorination Reactions

This reaction module describes dechlorination of 1,1,1,2-tetrachloroethane, tetrachloroethene, and related daughter products (including 1,1,1-TCA and 1,1-DCA) using first-order rate expressions. The module includes abiotic, aerobic, and anoxic/anaerobic reaction pathways, which the user may selectively turn off by setting the (spatially variable) values of the stoichiometric yields and/or the reaction rate constants to zero. See the section on RT3D MNA/EA Reaction Module Commonalities and the Discussion of Select Reaction Parameters for additional information on features common to all of these MNA/EA reaction modules and explanation of key reaction parameters.

Table 24 lists the chemical species included in this reaction module. Dechlorination reactions for chlorinated ethane contaminants can result in formation of chlorinated ethene species, so this reaction module combines the reaction pathways for these two groups of contaminants. Figure 20 shows the conceptual model describing the potential biotic and abiotic degradation pathways of both chlorinated ethene and chlorinated ethane contaminants. See the conceptual model discussion for the Mixed Chloroethene/ Chloroethane/Chloromethane Dechlorination reaction module for information on the development of the reaction pathways and the assumption of first-order reaction kinetics.

Table 24. Chemical Species Included in the Dechlorination of 1,1,1,2-Tetrachloroethane and Chloroethenes Reaction Module

No.	Abbreviation ^a	Chemical Name	Selected Alternate Name	CAS ^b Registry Number	Molecular Weight ^c (g/mol)	Chemical Formula
1	TeCA	1,1,1,2-Tetrachloroethane	1,1,1,2-TeCA		167.84928	C ₂ H ₂ Cl ₄
2	TCA	1,1,1-Trichloroethane	1,1,1-TCA		133.40422	C ₂ H ₃ Cl ₃
3	DCA	1,1-Dichloroethane	1,1-DCA		98.95916	C ₂ H ₄ Cl ₂
4	CA	Chloroethane	Ethyl Chloride	75-00-3	64.5141	C ₂ H ₅ Cl
5	PCE	Tetrachloroethene	Tetrachloroethylene; Perchloroethylene	127-18-4	165.8334	C ₂ Cl ₄
6	TCE	Trichloroethene	Trichloroethylene	79-01-6	131.38834	C ₂ HCl ₃
7	cDCE	cis-1,2-Dichloroethene	cis-1,2-Dichloroethylene; cis-1,2-DCE; cis-DCE	156-59-2	96.94328	C ₂ H ₂ Cl ₂
8	tDCE	trans-1,2-Dichloroethene	trans-1,2-Dichloroethylene; trans-1,2-DCE; trans-DCE	156-60-5	96.94328	C ₂ H ₂ Cl ₂
9	11DCE	1,1-Dichloroethene	Vinylidene Chloride; 1,1-DCE	75-35-4	96.94328	C ₂ H ₂ Cl ₂
10	VC	Chloroethene	Vinyl Chloride	75-01-4	62.49822	C ₂ H ₃ Cl
11	Tracer	Conservative Tracer	—	N/A	N/A	N/A

^a These abbreviations refer to the specific chemicals listed here and should not be confused with different chemicals that may use the same abbreviation in other reaction modules.

^b CAS = Chemical Abstracts Service (see <http://www.cas.org/EO/regsys.html>)

^c Based on International Union of Pure and Applied Chemistry values reported by Loss [2003].

N/A – Not Applicable

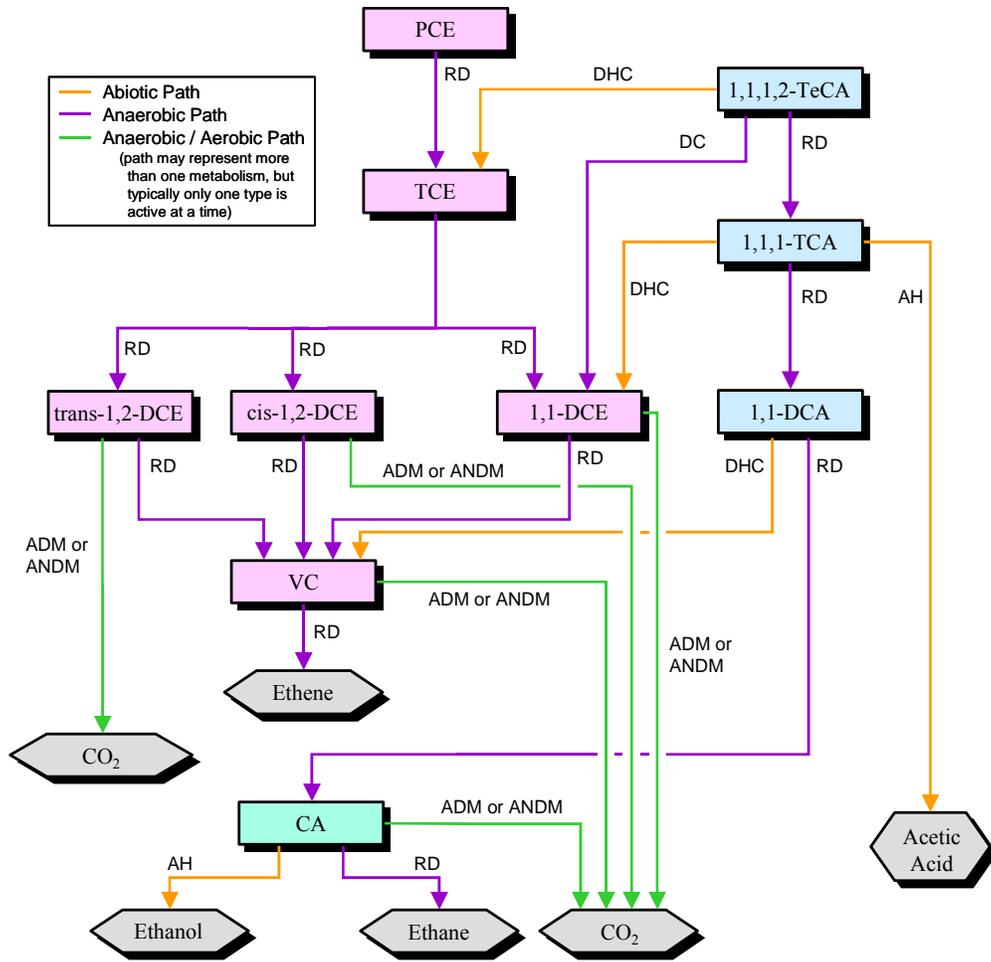


Figure 20. Conceptual Model for Dechlorination Reactions in the Dechlorination of 1,1,1,2-Tetrachloroethane and Chloroethenes Reaction Module — Species in hexagonal shaded boxes are innocuous products and are not tracked in the reaction module. The reaction types for each pathway are described in Table 3.

5.2 Reaction Equations

The set of ODEs comprising this reaction module are shown in Equations 57 to 67. These ODEs describe the reaction kinetics for the 11 chemical species in Table 24. See Table 25 for a detailed itemization of all reaction parameters used in this reaction module.

$$\frac{dC_{TeCA}}{dt} = \left(-kan_{TeCA} \cdot C_{TeCA} - kab_{TeCA} \cdot C_{TeCA} \right) \quad (57)$$

$$\frac{dC_{TCA}}{dt} = \left(Y_{TCA} \cdot Fan_{TCA} \cdot kan_{TeCA} \cdot C_{TeCA} - kan_{TCA} \cdot C_{TCA} - kab_{TCA} \cdot C_{TCA} \right) \quad (58)$$

$$\frac{dC_{DCA}}{dt} = \begin{pmatrix} \frac{Y_{DCA}}{TCA} \cdot kan_{TCA} \cdot C_{TCA} \\ - kan_{DCA} \cdot C_{DCA} - kab_{DCA} \cdot C_{DCA} \end{pmatrix} \quad (59)$$

$$\frac{dC_{CA}}{dt} = \begin{pmatrix} \frac{Y_{CA}}{DCA} \cdot kan_{DCA} \cdot C_{DCA} \\ - kan_{CA} \cdot C_{CA} - kab_{CA} \cdot C_{CA} - kae_{CA} \cdot C_{CA} \end{pmatrix} \quad (60)$$

$$\frac{dC_{PCE}}{dt} = \begin{pmatrix} - kan_{PCE} \cdot C_{PCE} \end{pmatrix} \quad (61)$$

$$\frac{dC_{TCE}}{dt} = \begin{pmatrix} \frac{Y_{TCE}}{PCE} \cdot kan_{PCE} \cdot C_{PCE} \\ + \frac{Y_{TCE}}{TeCA} \cdot kab_{TeCA} \cdot C_{TeCA} - kan_{TCE} \cdot C_{TCE} \end{pmatrix} \quad (62)$$

$$\frac{dC_{cDCE}}{dt} = \begin{pmatrix} \frac{Y_{DCE}}{TCE} \cdot Fan_{cDCE} \cdot \frac{kan_{TCE}}{TCE} \cdot C_{TCE} \\ - kan_{cDCE} \cdot C_{cDCE} - kae_{cDCE} \cdot C_{cDCE} \end{pmatrix} \quad (63)$$

$$\frac{dC_{iDCE}}{dt} = \begin{pmatrix} \frac{Y_{DCE}}{TCE} \cdot Fan_{iDCE} \cdot \frac{kan_{TCE}}{TCE} \cdot C_{TCE} \\ - kan_{iDCE} \cdot C_{iDCE} - kae_{iDCE} \cdot C_{iDCE} \end{pmatrix} \quad (64)$$

$$\frac{dC_{11DCE}}{dt} = \begin{pmatrix} \frac{Y_{DCE}}{TCE} \cdot Fan_{11DCE} \cdot \frac{kan_{TCE}}{TCE} \cdot C_{TCE} + \frac{Y_{DCE}}{TeCA} \cdot Fan_{11DCE} \cdot \frac{kan_{TeCA}}{TeCA} \cdot C_{TeCA} \\ + \frac{Y_{DCE}}{TCA} \cdot Fab_{11DCE} \cdot \frac{kab_{TCA}}{TCA} \cdot C_{TCA} \\ - kan_{11DCE} \cdot C_{11DCE} - kae_{11DCE} \cdot C_{11DCE} \end{pmatrix} \quad (65)$$

$$\frac{dC_{VC}}{dt} = \left(\begin{array}{l} \frac{Y_{VC}}{DCE} \cdot Fan_{cDCE} \cdot \frac{VC}{cDCE} \cdot kan_{cDCE} \cdot C_{cDCE} \\ + \frac{Y_{VC}}{DCE} \cdot Fan_{iDCE} \cdot \frac{VC}{iDCE} \cdot kan_{iDCE} \cdot C_{iDCE} \\ + \frac{Y_{VC}}{DCE} \cdot Fan_{11DCE} \cdot \frac{VC}{11DCE} \cdot kan_{11DCE} \cdot C_{11DCE} \\ + \frac{Y_{VC}}{DCA} \cdot kab_{DCA} \cdot C_{DCA} \\ - kan_{VC} \cdot C_{VC} - kae_{VC} \cdot C_{VC} \end{array} \right) \quad (66)$$

$$\frac{dC_{Tracer}}{dt} = 0.0 \quad (\text{Conservative [non-reactive] tracer.}) \quad (67)$$

The first-order decay rate constants [T^{-1}] of the i^{th} species are represented in the equations above by the kan_i , kae_i , and kab_i terms for anaerobic biological reactions, aerobic biological reactions, or abiotic reactions, respectively. The concentration of the i^{th} species is represented by the C_i term [ML^{-3}]. The R_i terms represent the retardation factor for the i^{th} species [unitless].

In cases where multiple daughter products may be produced from dechlorination of a single parent species, the amount of each daughter species that is produced is a function of a mass yield [MM^{-1}] and a stoichiometric dechlorination yield [mol/mol]. The mass yield value, $Y_{d/p}$, accounts for the difference in molecular weight between the parent species "p" and the daughter species "d." All isomers of a daughter chemical have the same mass yield. Mass yield values are included in the reaction module code and do not need to be input by the user. The stoichiometric dechlorination yield represents the site-specific stoichiometry for each reaction pathway that occurs as either an anaerobic ($Fan_{d/p}$) or an abiotic process ($Fab_{d/p}$). The stoichiometric dechlorination yield is the fractional moles of daughter species that are produced by dechlorination of one mole of the parent species. The net yield is the product of the mass yield and the stoichiometric dechlorination yield. To preserve the mass balance, the values of the stoichiometric dechlorination yields are constrained by the relations in Equations 68 to 73.

$$Fan_{\frac{TCA}{TeCA}} + Fan_{\frac{11DCE}{TeCA}} = 1.0 \quad (68)$$

$$Fab_{\frac{11DCE}{TCA}} \leq 1.0 \quad (69)$$

$$Fan_{\frac{cDCE}{TCE}} + Fan_{\frac{iDCE}{TCE}} + Fan_{\frac{11DCE}{TCE}} = 1.0 \quad (70)$$

$$Fan \frac{VC}{cDCE} \leq 1.0 \quad (71)$$

$$Fan \frac{VC}{iDCE} \leq 1.0 \quad (72)$$

$$Fan \frac{VC}{11DCE} \leq 1.0 \quad (73)$$

5.3 Required Input

The reaction parameters for this reaction module are made available to RT3D as part of the input for the Reaction Package. The Reaction Package input file structure is discussed in the RT3D manual and addendum [Clement, 1997; Clement and Johnson, 2002]. The 28 reaction parameters that must be specified for this reaction module are listed in Table 25 in the required order (ID Number) with units and a description. Site-specific knowledge from field data or laboratory tests should be applied to determine an appropriate model configuration for reaction parameters (i.e., the values and the spatial distribution).

Table 25. *Input Parameters for the Dechlorination of 1,1,1,2-Tetrachloroethane and Chloroethenes Reaction Module*

ID #	Parameter	Fortran Variable	Units	Description
1	$Fab \frac{11DCE}{TCA}$	fab_11dce_tca	mol/mol	Moles of 1,1-DCE produced from abiotic decay of one mole of TCA
2	$Fan \frac{TCA}{TeCA}$	fan_tca_teca	mol/mol	Moles of TCA produced from anaerobic decay of one mole of TeCA
3	$Fan \frac{11DCE}{TeCA}$	fan_11dce_teca	mol/mol	Moles of 1,1-DCE produced from anaerobic decay of one mole of TeCA
4	$Fan \frac{cDCE}{TCE}$	fan_cdce_tce	mol/mol	Moles of cis-1,2-DCE produced from anaerobic decay of one mole of TCE
5	$Fan \frac{iDCE}{TCE}$	fan_tdce_tce	mol/mol	Moles of trans-1,2-DCE produced from anaerobic decay of one mole of TCE
6	$Fan \frac{11DCE}{TCE}$	fan_11dce_tce	mol/mol	Moles of 1,1-DCE produced from anaerobic decay of one mole of TCE
7	$Fan \frac{VC}{cDCE}$	fan_vc_cdce	mol/mol	Moles of VC produced from anaerobic decay of one mole of cis-1,2-DCE
8	$Fan \frac{VC}{iDCE}$	fan_vc_tdce	mol/mol	Moles of VC produced from anaerobic decay of one mole of trans-1,2-DCE

Table 25. (contd)

ID #	Parameter	Fortran Variable	Units	Description
9	$Fan_{\frac{VC}{1,1DCE}}$	fan_vc_11dce	mol/mol	Moles of VC produced from anaerobic decay of one mole of 1,1-DCE
10	kab_{TeCA}	kab_teca	1/day	First-order decay coefficient for abiotic dechlorination of TeCA
11	kab_{TCA}	kab_tca	1/day	First-order decay coefficient for abiotic dechlorination of TCA
12	kab_{DCA}	kab_dca	1/day	First-order decay coefficient for abiotic dechlorination of DCA
13	kab_{CA}	kab_ca	1/day	First-order decay coefficient for abiotic dechlorination of CA
14	kan_{TeCA}	kan_teca	1/day	First-order decay coefficient for anaerobic dechlorination of TeCA
15	kan_{TCA}	kan_tca	1/day	First-order decay coefficient for anaerobic dechlorination of TCA
16	kan_{DCA}	kan_dca	1/day	First-order decay coefficient for anaerobic dechlorination of DCA
17	kan_{CA}	kan_ca	1/day	First-order decay coefficient for anaerobic dechlorination of CA
18	kan_{PCE}	kan_pce	1/day	First-order decay coefficient for anaerobic dechlorination of PCE
19	kan_{TCE}	kan_tce	1/day	First-order decay coefficient for anaerobic dechlorination of TCE
20	kan_{cDCE}	kan_cdce	1/day	First-order decay coefficient for anaerobic dechlorination of cis-1,2-DCE
21	kan_{tDCE}	kan_tdce	1/day	First-order decay coefficient for anaerobic dechlorination of trans-1,2-DCE
22	$kan_{1,1DCE}$	kan_11dce	1/day	First-order decay coefficient for anaerobic dechlorination of 1,1-DCE
23	kan_{VC}	kan_vc	1/day	First-order decay coefficient for anaerobic dechlorination of VC
24	kae_{CA}	kae_ca	1/day	First-order decay coefficient for aerobic dechlorination of CA
25	kae_{cDCE}	kae_cdce	1/day	First-order decay coefficient for aerobic dechlorination of cis-1,2-DCE
26	kae_{tDCE}	kae_tdce	1/day	First-order decay coefficient for aerobic dechlorination of trans-1,2-DCE
27	$kae_{1,1DCE}$	kae_11dce	1/day	First-order decay coefficient for aerobic dechlorination of 1,1-DCE
28	kae_{VC}	kae_vc	1/day	First-order decay coefficient for aerobic dechlorination of VC

5.4 Example Simulations

Simulations with this reaction module were conducted with RT3D in a batch reactor (no flow) mode to show examples of how the reaction module simulates the pattern of dechlorination. The parameter values for each example simulation are listed in Tables 26 through 29. These

parameters are arbitrary values and are not directly related to any specific laboratory data. Site-specific values would need to be determined as part of a calibration process. Results for these example batch simulations are shown in the Figures 21 through 24, respectively.

Table 26. *Parameter Values for Example Simulation 1 – Base Case Anaerobic Conditions – with the Dechlorination of 1,1,1,2-Tetrachloroethane and Chloroethenes Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fab_11dce_tca	0.2	mol/mol	15	kan_tca	0.01	1/day
2	fan_tca_teca	0.2	mol/mol	16	kan_dca	0.025	1/day
3	fan_11dce_teca	0.8	mol/mol	17	kan_ca	0.025	1/day
4	fan_cdce_tce	0.8	mol/mol	18	kan_pce	0.025	1/day
5	fan_tdce_tce	0.2	mol/mol	19	kan_tce	0.025	1/day
6	fan_11dce_tce	0	mol/mol	20	kan_cdce	0.025	1/day
7	fan_vc_cdce	0.8	mol/mol	21	kan_tdce	0.025	1/day
8	fan_vc_tdce	0.8	mol/mol	22	kan_11dce	0.025	1/day
9	fan_vc_11dce	0.8	mol/mol	23	kan_vc	0.0025	1/day
10	kab_teca	0.006	1/day	24	kae_ca	0	1/day
11	kab_tca	0	1/day	25	kae_cdce	0	1/day
12	kab_dca	0.00003	1/day	26	kae_tdce	0	1/day
13	kab_ca	0.001	1/day	27	kae_11dce	0	1/day
14	kan_teca	0.005	1/day	28	kae_vc	0	1/day

Table 27. *Parameter Values for Example Simulation 2 – Rates at 10% of Example Simulation 1 – with the Dechlorination of 1,1,1,2-Tetrachloroethane and Chloroethenes Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fab_11dce_tca	0.2	mol/mol	15	kan_tca	0.001	1/day
2	fan_tca_teca	0.2	mol/mol	16	kan_dca	0.0025	1/day
3	fan_11dce_teca	0.8	mol/mol	17	kan_ca	0.0025	1/day
4	fan_cdce_tce	0.8	mol/mol	18	kan_pce	0.0025	1/day
5	fan_tdce_tce	0.2	mol/mol	19	kan_tce	0.0025	1/day
6	fan_11dce_tce	0	mol/mol	20	kan_cdce	0.0025	1/day
7	fan_vc_cdce	0.8	mol/mol	21	kan_tdce	0.0025	1/day
8	fan_vc_tdce	0.8	mol/mol	22	kan_11dce	0.0025	1/day
9	fan_vc_11dce	0.8	mol/mol	23	kan_vc	0.00025	1/day
10	kab_teca	0.0006	1/day	24	kae_ca	0	1/day
11	kab_tca	0	1/day	25	kae_cdce	0	1/day
12	kab_dca	0.000003	1/day	26	kae_tdce	0	1/day
13	kab_ca	0.0001	1/day	27	kae_11dce	0	1/day
14	kan_teca	0.0005	1/day	28	kae_vc	0	1/day

Table 28. Parameter Values for Example Simulation 3 – Different F Values Than Example Simulation 1 – with the Dechlorination of 1,1,1,2-Tetrachloroethane and Chloroethenes Reaction Module

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fab_11dce_tca	0.8	mol/mol	15	kan_tca	0.01	1/day
2	fan_tca_teca	0.2	mol/mol	16	kan_dca	0.025	1/day
3	fan_11dce_teca	0.8	mol/mol	17	kan_ca	0.025	1/day
4	fan_cdce_tce	0.2	mol/mol	18	kan_pce	0.025	1/day
5	fan_tdce_tce	0	mol/mol	19	kan_tce	0.025	1/day
6	fan_11dce_tce	0.8	mol/mol	20	kan_cdce	0.025	1/day
7	fan_vc_cdce	0.2	mol/mol	21	kan_tdce	0.025	1/day
8	fan_vc_tdce	0.2	mol/mol	22	kan_11dce	0.025	1/day
9	fan_vc_11dce	0.2	mol/mol	23	kan_vc	0.0025	1/day
10	kab_teca	0.006	1/day	24	kae_ca	0	1/day
11	kab_tca	0	1/day	25	kae_cdce	0	1/day
12	kab_dca	0.00003	1/day	26	kae_tdce	0	1/day
13	kab_ca	0.001	1/day	27	kae_11dce	0	1/day
14	kan_teca	0.005	1/day	28	kae_vc	0	1/day

Table 29. Parameter Values for Example Simulation 4 – Base Case Aerobic Conditions – with the Dechlorination of 1,1,1,2-Tetrachloroethane and Chloroethenes Reaction Module

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fab_11dce_tca	0.2	mol/mol	15	kan_tca	0	1/day
2	fan_tca_teca	0	mol/mol	16	kan_dca	0	1/day
3	fan_11dce_teca	0	mol/mol	17	kan_ca	0	1/day
4	fan_cdce_tce	0	mol/mol	18	kan_pce	0	1/day
5	fan_tdce_tce	0	mol/mol	19	kan_tce	0	1/day
6	fan_11dce_tce	0	mol/mol	20	kan_cdce	0	1/day
7	fan_vc_cdce	0	mol/mol	21	kan_tdce	0	1/day
8	fan_vc_tdce	0	mol/mol	22	kan_11dce	0	1/day
9	fan_vc_11dce	0	mol/mol	23	kan_vc	0	1/day
10	kab_teca	0.006	1/day	24	kae_ca	0.005	1/day
11	kab_tca	0	1/day	25	kae_cdce	0.005	1/day
12	kab_dca	0.00003	1/day	26	kae_tdce	0.005	1/day
13	kab_ca	0.001	1/day	27	kae_11dce	0.005	1/day
14	kan_teca	0	1/day	28	kae_vc	0.005	1/day

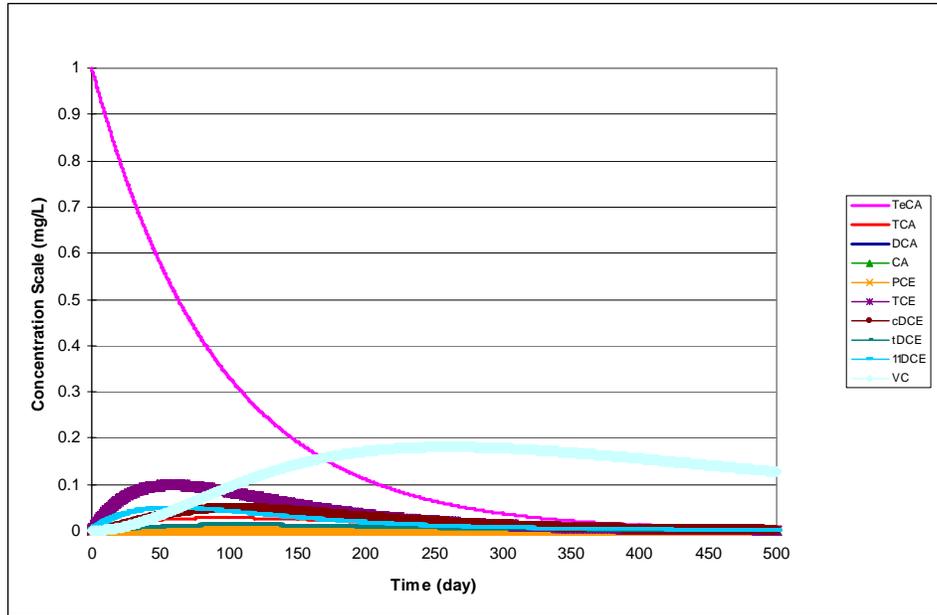


Figure 21. Dechlorination of 1,1,1,2-TeCA Using the Parameter Values Shown in Table 26 — The initial concentration for TeCA was 1 mg/L. All other species concentrations started at zero.

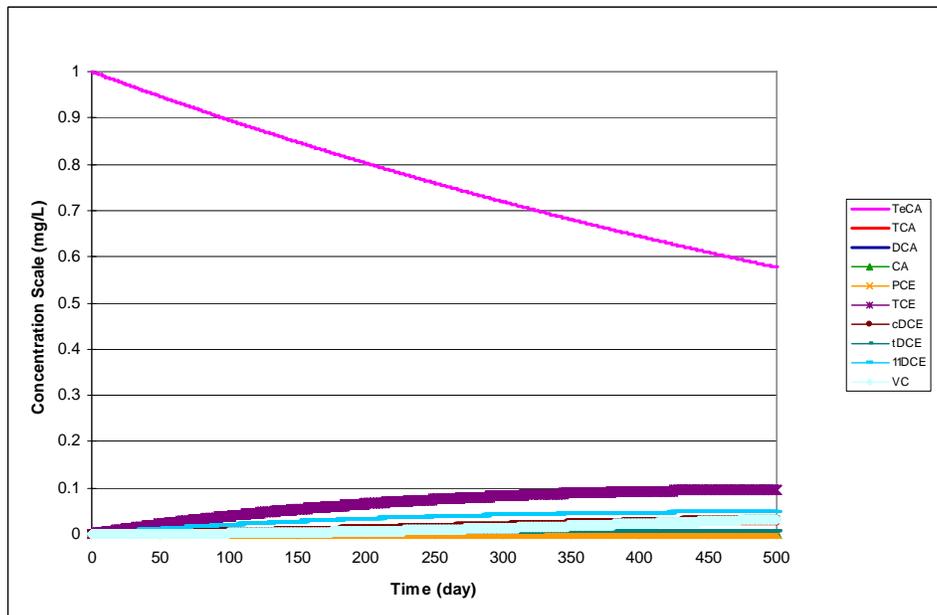


Figure 22. Dechlorination of 1,1,1,2-TeCA Using the Parameter Values Shown in Table 27 — The initial concentration for TeCA was 1 mg/L. All other species concentrations started at zero.

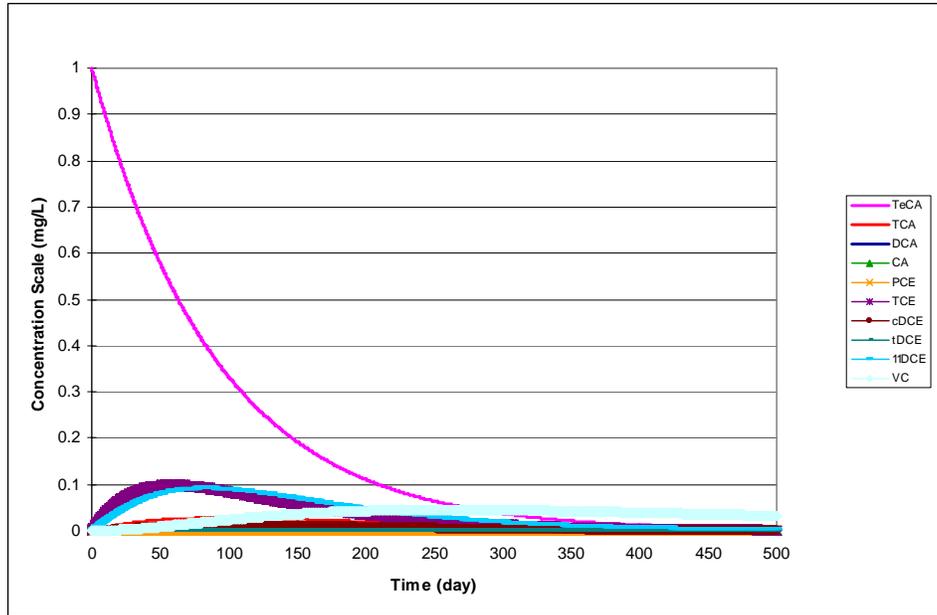


Figure 23. Dechlorination of 1,1,1,2-TeCA Using the Parameter Values Shown in Table 28 — The initial concentration for TeCA was 1 mg/L. All other species concentrations started at zero.

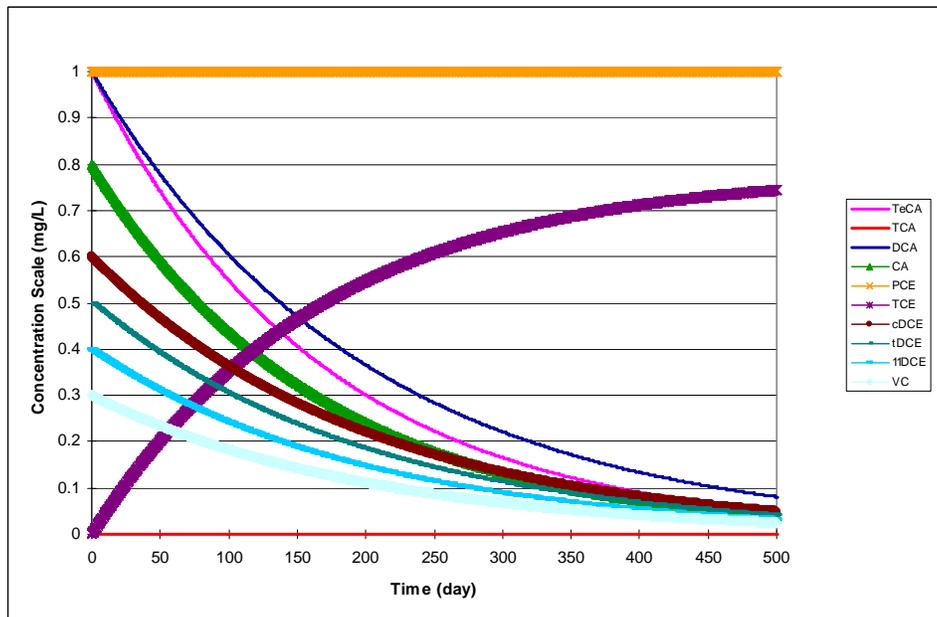


Figure 24. Aerobic and Abiotic Degradation of Contaminants in the 1,1,1,2-TeCA and PCE Families Using the Parameter Values Shown in Table 29 — The initial concentrations for TeCA, TCA, DCA, CA, PCE, TCE, cDCE, tDCE, 11DCE, and VC were 1, 0, 1, 0.8, 1, 0, 0.6, 0.5, 0.4, and 0.3 mg/L, respectively.

6.0 Chloroethene Dechlorination

6.1 Conceptual Model for Dechlorination Reactions

This reaction module describes dechlorination of tetrachloroethene, and related daughter products using first-order rate expressions. The module includes both aerobic and anoxic/anaerobic reaction pathways, which the user may selectively turn off by setting the (spatially variable) values of the stoichiometric yields and/or the reaction rate constants to zero. See the section on RT3D MNA/EA Reaction Module Commonalities and the Discussion of Select Reaction Parameters for additional information on features common to all of these MNA/EA reaction modules and explanation of key reaction parameters.

Table 30 lists the chemical species included in this reaction module. Figure 25 shows the conceptual model describing the potential biotic degradation pathways of both chlorinated ethene contaminants. Note that abiotic degradation reactions for chlorinated ethene compounds are negligible, thus they are not included. See the conceptual model discussion for the Mixed Chloroethene/ Chloroethane/Chloromethane Dechlorination reaction module for information on the development of the reaction pathways and the assumption of first-order reaction kinetics.

Table 30. Chemical Species Included in the Chloroethene Dechlorination Reaction Module

No.	Abbreviation ^a	Chemical Name	Selected Alternate Name	CAS ^b Registry Number	Molecular Weight ^c (g/mol)	Chemical Formula
1	PCE	Tetrachloroethene	Tetrachloroethylene; Perchloroethylene	127-18-4	165.8334	C ₂ Cl ₄
2	TCE	Trichloroethene	Trichloroethylene	79-01-6	131.38834	C ₂ HCl ₃
3	cDCE	cis-1,2-Dichloroethene	cis-1,2-Dichloroethylene; cis-1,2-DCE; cis-DCE	156-59-2	96.94328	C ₂ H ₂ Cl ₂
4	tDCE	trans-1,2-Dichloroethene	trans-1,2-Dichloroethylene; trans-1,2-DCE; trans-DCE	156-60-5	96.94328	C ₂ H ₂ Cl ₂
5	11DCE	1,1-Dichloroethene	Vinylidene Chloride; 1,1-DCE	75-35-4	96.94328	C ₂ H ₂ Cl ₂
6	VC	Chloroethene	Vinyl Chloride	75-01-4	62.49822	C ₂ H ₃ Cl
7	Tracer	Conservative Tracer	—	N/A	N/A	N/A

^a These abbreviations refer to the specific chemicals listed here and should not be confused with different chemicals that may use the same abbreviation in other reaction modules.

^b CAS = Chemical Abstracts Service (see <http://www.cas.org/EO/regsys.html>)

^c Based on International Union of Pure and Applied Chemistry values reported by Loss [2003].

N/A – Not Applicable

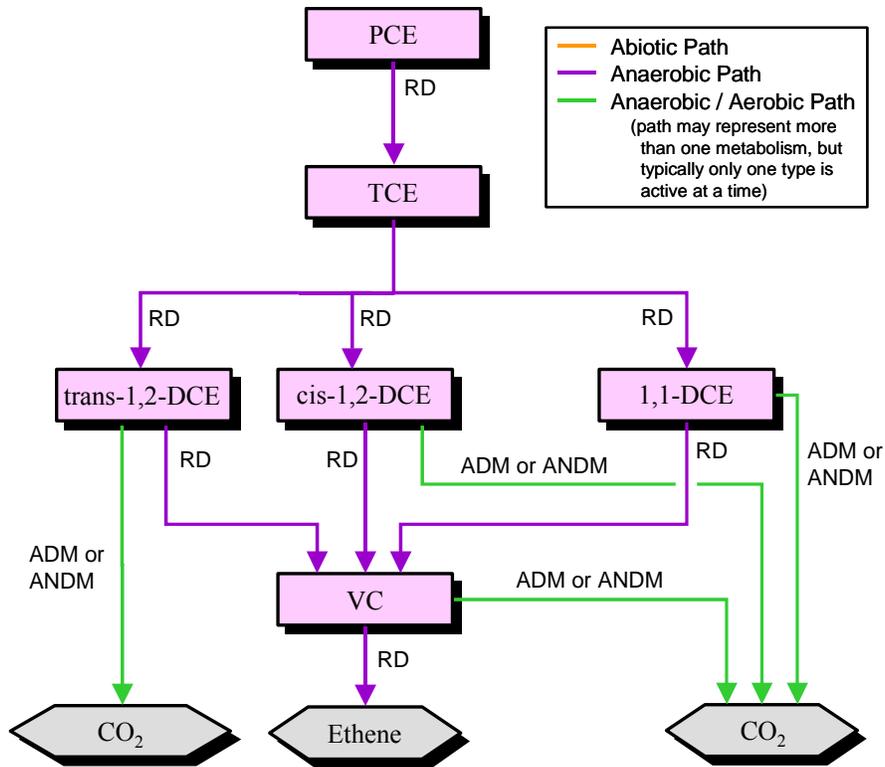


Figure 25. *Conceptual Model for Dechlorination Reactions in the Chloroethene Dechlorination Reaction Module — Species in hexagonal shaded boxes are innocuous products and are not tracked in the reaction module. The reaction types for each pathway are described in Table 3.*

6.2 Reaction Equations

The set of ODEs comprising this reaction module are shown in Equations 74 to 80. These ODEs describe the reaction kinetics for the 7 chemical species in Table 30. See Table 31 for a detailed itemization of all reaction parameters used in this reaction module.

$$\frac{dC_{PCE}}{dt} = \left(-kan_{PCE} \cdot C_{PCE} \right) \quad (74)$$

$$\frac{dC_{TCE}}{dt} = \left(\begin{array}{c} Y_{TCE/PCE} \cdot kan_{PCE} \cdot C_{PCE} \\ - kan_{TCE} \cdot C_{TCE} \end{array} \right) \quad (75)$$

$$\frac{dC_{cDCE}}{dt} = \left(\begin{array}{l} \frac{Y_{DCE}}{TCE} \cdot Fan_{cDCE} \cdot kan_{TCE} \cdot C_{TCE} \\ - kan_{cDCE} \cdot C_{cDCE} - kae_{cDCE} \cdot C_{cDCE} \end{array} \right) \quad (76)$$

$$\frac{dC_{iDCE}}{dt} = \left(\begin{array}{l} \frac{Y_{DCE}}{TCE} \cdot Fan_{iDCE} \cdot kan_{TCE} \cdot C_{TCE} \\ - kan_{iDCE} \cdot C_{iDCE} - kae_{iDCE} \cdot C_{iDCE} \end{array} \right) \quad (77)$$

$$\frac{dC_{11DCE}}{dt} = \left(\begin{array}{l} \frac{Y_{DCE}}{TCE} \cdot Fan_{11DCE} \cdot kan_{TCE} \cdot C_{TCE} \\ - kan_{11DCE} \cdot C_{11DCE} - kae_{11DCE} \cdot C_{11DCE} \end{array} \right) \quad (78)$$

$$\frac{dC_{VC}}{dt} = \left(\begin{array}{l} \frac{Y_{VC}}{DCE} \cdot Fan_{VC} \cdot kan_{cDCE} \cdot C_{cDCE} \\ + \frac{Y_{VC}}{DCE} \cdot Fan_{VC} \cdot kan_{iDCE} \cdot C_{iDCE} \\ + \frac{Y_{VC}}{DCE} \cdot Fan_{VC} \cdot kan_{11DCE} \cdot C_{11DCE} \\ - kan_{VC} \cdot C_{VC} - kae_{VC} \cdot C_{VC} \end{array} \right) \quad (79)$$

$$\frac{dC_{Tracer}}{dt} = 0.0 \quad (Conservative [non-reactive] tracer.) \quad (80)$$

The first-order decay rate constants [T^{-1}] of the i^{th} species are represented in the equations above by the kan_i , kae_i , and kab_i terms for anaerobic biological reactions, aerobic biological reactions, or abiotic reactions, respectively. The concentration of the i^{th} species is represented by the C_i term [ML^{-3}]. The R_i terms represent the retardation factor for the i^{th} species [unitless].

In cases where multiple daughter products may be produced from dechlorination of a single parent species, the amount of each daughter species that is produced is a function of a mass yield [MM^{-1}] and a stoichiometric dechlorination yield [mol/mol]. The mass yield value, $Y_{d/p}$, accounts for the difference in molecular weight between the parent species "p" and the daughter species "d." All isomers of a daughter chemical have the same mass yield. Mass yield values are included in the reaction module code and do not need to be input by the user. The stoichiometric dechlorination yield represents the site-specific stoichiometry for each reaction pathway that occurs as either an anaerobic ($Fan_{d/p}$) or an abiotic process ($Fab_{d/p}$). The

stoichiometric dechlorination yield is the fractional moles of daughter species that are produced by dechlorination of one mole of the parent species. The net yield is the product of the mass yield and the stoichiometric dechlorination yield. To preserve the mass balance, the values of the stoichiometric dechlorination yields are constrained by the relations in Equations 81 to 84.

$$Fan_{\frac{cDCE}{TCE}} + Fan_{\frac{idCE}{TCE}} + Fan_{\frac{DCE11}{TCE}} = 1.0 \quad (81)$$

$$Fan_{\frac{VC}{cDCE}} \leq 1.0 \quad (82)$$

$$Fan_{\frac{VC}{idCE}} \leq 1.0 \quad (83)$$

$$Fan_{\frac{VC}{DCE11}} \leq 1.0 \quad (84)$$

6.3 Required Input

The reaction parameters for this reaction module are made available to RT3D as part of the input for the Reaction Package. The Reaction Package input file structure is discussed in the RT3D manual and addendum [Clement, 1997; Clement and Johnson, 2002]. The 16 reaction parameters that must be specified for this reaction module are listed in Table 31 in the required order (ID Number) with units and a description. Site-specific knowledge from field data or laboratory tests should be applied to determine an appropriate model configuration for reaction parameters (i.e., the values and the spatial distribution).

Table 31. Input Parameters for the Chloroethene Dechlorination Reaction Module

ID #	Parameter	Fortran Variable	Units	Description
1	$Fan_{\frac{cDCE}{TCE}}$	fan_cdce_tce	mol/mol	Moles of cis-1,2-DCE produced from anaerobic decay of one mole of TCE
2	$Fan_{\frac{iDCE}{TCE}}$	fan_tdce_tce	mol/mol	Moles of trans-1,2-DCE produced from anaerobic decay of one mole of TCE
3	$Fan_{\frac{11DCE}{TCE}}$	fan_11dce_tce	mol/mol	Moles of 1,1-DCE produced from anaerobic decay of one mole of TCE
4	$Fan_{\frac{VC}{cDCE}}$	fan_vc_cdce	mol/mol	Moles of VC produced from anaerobic decay of one mole of cis-1,2-DCE
5	$Fan_{\frac{VC}{iDCE}}$	fan_vc_tdce	mol/mol	Moles of VC produced from anaerobic decay of one mole of trans-1,2-DCE
6	$Fan_{\frac{VC}{11DCE}}$	fan_vc_11dce	mol/mol	Moles of VC produced from anaerobic decay of one mole of 1,1-DCE
7	kan_{PCE}	kan_pce	1/day	First-order decay coefficient for anaerobic dechlorination of PCE
8	kan_{TCE}	kan_tce	1/day	First-order decay coefficient for anaerobic dechlorination of TCE
9	kan_{cDCE}	kan_cdce	1/day	First-order decay coefficient for anaerobic dechlorination of cis-1,2-DCE
10	kan_{iDCE}	kan_tdce	1/day	First-order decay coefficient for anaerobic dechlorination of trans-1,2-DCE
11	kan_{11DCE}	kan_11dce	1/day	First-order decay coefficient for anaerobic dechlorination of 1,1-DCE
12	kan_{VC}	kan_vc	1/day	First-order decay coefficient for anaerobic dechlorination of VC
13	kae_{cDCE}	kae_cdce	1/day	First-order decay coefficient for aerobic dechlorination of cis-1,2-DCE
14	kae_{iDCE}	kae_tdce	1/day	First-order decay coefficient for aerobic dechlorination of trans-1,2-DCE
15	kae_{11DCE}	kae_11dce	1/day	First-order decay coefficient for aerobic dechlorination of 1,1-DCE
16	kae_{VC}	kae_vc	1/day	First-order decay coefficient for aerobic dechlorination of VC

6.4 Example Simulations

Simulations with this reaction module were conducted with RT3D in a batch reactor (no flow) mode to show examples of how the reaction module simulates the pattern of dechlorination. The parameter values for each example simulation are listed in Tables 32 through 35. These

parameters are arbitrary values and are not directly related to any specific laboratory data. Site-specific values would need to be determined as part of a calibration process. Results for these example batch simulations are shown in the Figures 26 through 29, respectively.

Table 32. *Parameter Values for Example Simulation 1 – Base Case Anaerobic Conditions – with the Chloroethene Dechlorination Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fan_cdce_tce	0.8	mol/mol	9	kan_cdce	0.005	1/day
2	fan_tdce_tce	0.2	mol/mol	10	kan_tdce	0.005	1/day
3	fan_11dce_tce	0	mol/mol	11	kan_11dce	0.005	1/day
4	fan_vc_cdce	0.8	mol/mol	12	kan_vc	0.0025	1/day
5	fan_vc_tdce	0.8	mol/mol	13	kae_cdce	0	1/day
6	fan_vc_11dce	0.8	mol/mol	14	kae_tdce	0	1/day
7	kan_pce	0.025	1/day	15	kae_11dce	0	1/day
8	kan_tce	0.025	1/day	16	kae_vc	0	1/day

Table 33. *Parameter Values for Example Simulation 2 – Rates at 10% of Example Simulation 1 – with the Chloroethene Dechlorination Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fan_cdce_tce	0.8	mol/mol	9	kan_cdce	0.0005	1/day
2	fan_tdce_tce	0.2	mol/mol	10	kan_tdce	0.0005	1/day
3	fan_11dce_tce	0	mol/mol	11	kan_11dce	0.0005	1/day
4	fan_vc_cdce	0.8	mol/mol	12	kan_vc	0.00025	1/day
5	fan_vc_tdce	0.8	mol/mol	13	kae_cdce	0	1/day
6	fan_vc_11dce	0.8	mol/mol	14	kae_tdce	0	1/day
7	kan_pce	0.0025	1/day	15	kae_11dce	0	1/day
8	kan_tce	0.0025	1/day	16	kae_vc	0	1/day

Table 34. *Parameter Values for Example Simulation 3 – Different F Values Than Example Simulation 1 – with the Chloroethene Dechlorination Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fan_cdce_tce	0.2	mol/mol	9	kan_cdce	0.005	1/day
2	fan_tdce_tce	0	mol/mol	10	kan_tdce	0.005	1/day
3	fan_11dce_tce	0.8	mol/mol	11	kan_11dce	0.005	1/day
4	fan_vc_cdce	0.2	mol/mol	12	kan_vc	0.0025	1/day
5	fan_vc_tdce	0.2	mol/mol	13	kae_cdce	0	1/day
6	fan_vc_11dce	0.2	mol/mol	14	kae_tdce	0	1/day
7	kan_pce	0.025	1/day	15	kae_11dce	0	1/day
8	kan_tce	0.025	1/day	16	kae_vc	0	1/day

Table 35. Parameter Values for Example Simulation 4 – Base Case Aerobic Conditions – with the Chloroethene Dechlorination Reaction Module

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	fan_cdce_tce	0	mol/mol	9	kan_cdce	0	1/day
2	fan_tdce_tce	0	mol/mol	10	kan_tdce	0	1/day
3	fan_11dce_tce	0	mol/mol	11	kan_11dce	0	1/day
4	fan_vc_cdce	0	mol/mol	12	kan_vc	0	1/day
5	fan_vc_tdce	0	mol/mol	13	kae_cdce	0.005	1/day
6	fan_vc_11dce	0	mol/mol	14	kae_tdce	0.005	1/day
7	kan_pce	0	1/day	15	kae_11dce	0.005	1/day
8	kan_tce	0	1/day	16	kae_vc	0.005	1/day

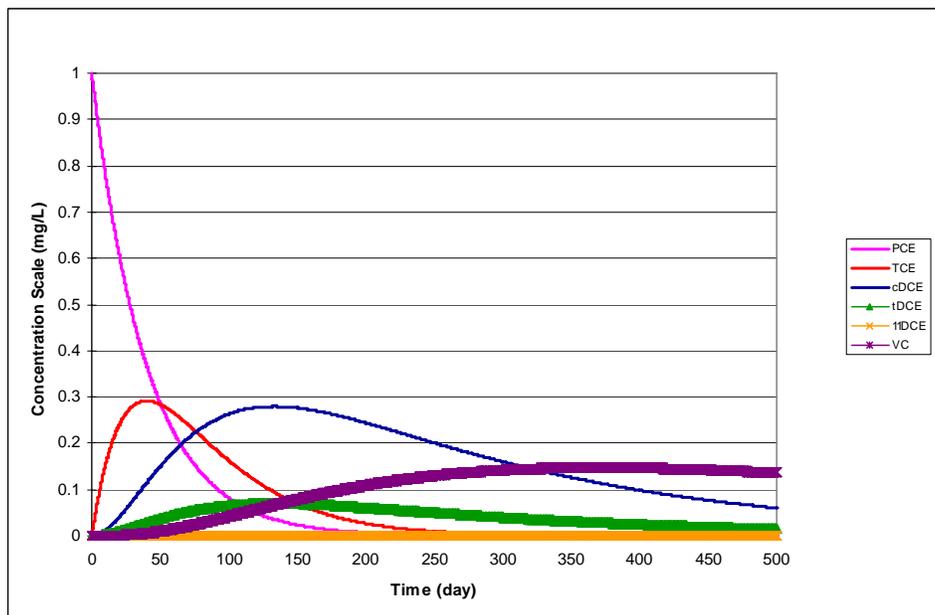


Figure 26. Dechlorination of PCE Using the Parameter Values Shown in Table 32 — The initial concentration for PCE was 1 mg/L. All other species concentrations started at zero.

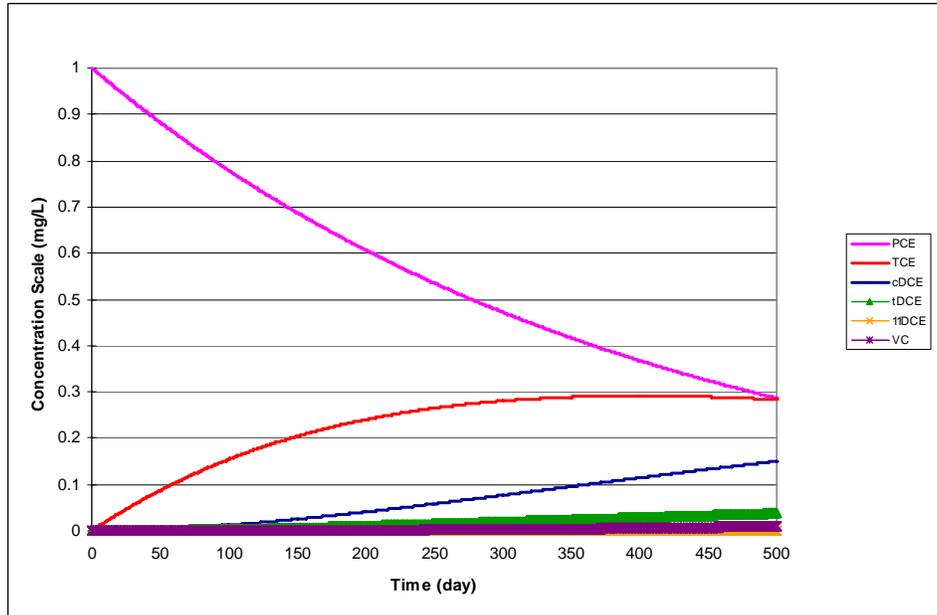


Figure 27. Dechlorination of PCE Using the Parameter Values Shown in Table 33 — The initial concentration for PCE was 1 mg/L. All other species concentrations started at zero.

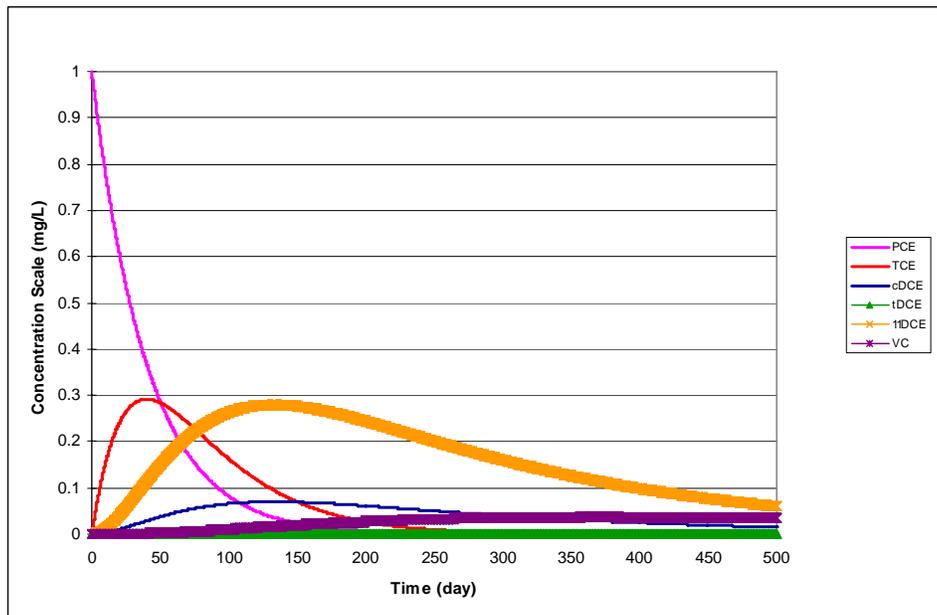


Figure 28. Dechlorination of PCE Using the Parameter Values Shown in Table 34 — The initial concentration for PCE was 1 mg/L. All other species concentrations started at zero.

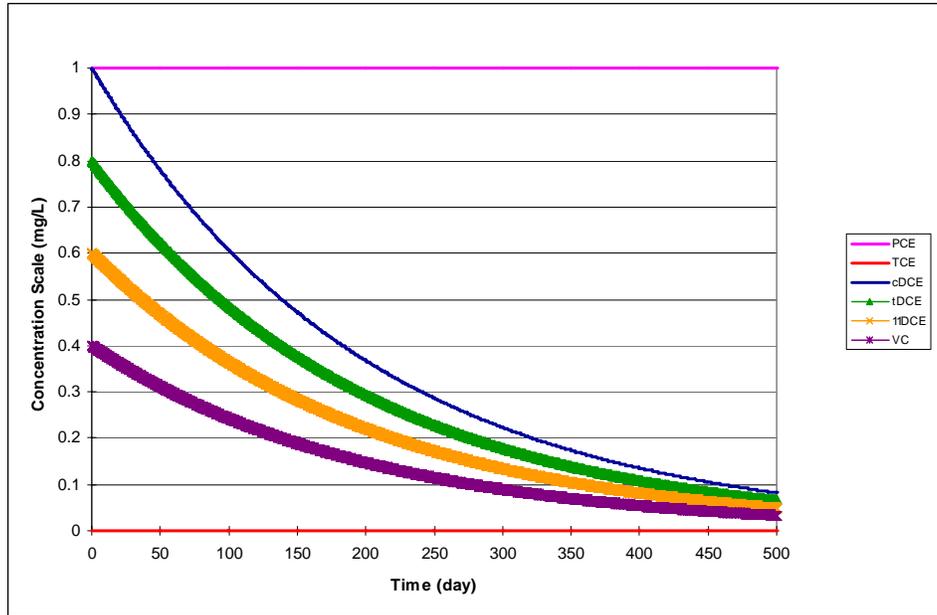


Figure 29. *Aerobic and Abiotic Degradation Using the Parameter Values Shown in Table 35 — The initial concentrations for PCE, TCE, cDCE, tDCE, 11DCE, and VC were 1, 0, 1, 0.8, 0.6, and 0.4 mg/L, respectively.*

7.0 Redox-Linked Dechlorination of Chloroethenes

7.1 Conceptual Model for Dechlorination Reactions

This reaction module describes dechlorination of chlorinated ethene compounds by natural attenuation processes where the pathway and rate of transformation is dependent on the oxidation-reduction conditions. The reaction module adjusts the rate of dechlorination based on a simplified framework to represent the oxidation-reduction conditions in the aquifer. This module enables the user to link dechlorination rate to the concentration of geochemical indicator species. The module is not a full geochemical model, but provides one potential means for the user to model dechlorination at sites where the oxidation-reduction conditions in the aquifer are spatially or temporally variable. The module includes both aerobic and anoxic/anaerobic reaction pathways using first-order rate expressions (see the conceptual model description of the Mixed Chloroethene/ Chloroethane/Chloromethane Dechlorination reaction module for discussion on the assumption of first-order reaction kinetics). When oxygen is present, aerobic dechlorination of DCE isomers and VC can occur. If the oxygen concentration is below 0.1 mg/L, aerobic dechlorination is inhibited. At low concentrations of oxygen (dependent on a user-specified oxygen inhibition coefficient), anoxic/anaerobic dechlorination pathways are possible with rates depending on the concentration of key redox couples. Nitrate and oxygen inhibit all of the anoxic/anaerobic dechlorination pathways. The three key redox couples included in the module are iron (ferrous iron/amorphous ferric hydroxide), sulfur (sulfate/sulfide), and methane (methane/CO₂). The redox conditions, as indicated by a calculated pE value, are based on the relative concentrations of these species in each grid cell. The reaction module is based on the assumption that the redox conditions related to the key redox couples control the dechlorination reaction rate. Biological activity is not modeled explicitly under the premise that the biological activity related to natural attenuation occurs based on the low, widely distributed concentration of indigenous bacteria at a rate dependent on the geochemical conditions. The concentration of bacteria is assumed to remain constant. If sufficient substrate is present at a site to drive bacterial growth dynamics, other reaction modules that consider biomass growth and subsequent impacts to dechlorination rate should be used.

The concentrations of redox couples can be set as initial conditions with any desired spatial distribution (e.g., by interpolation of data at multiple monitoring wells). The redox species concentrations can then either 1) stay static during the simulation, or 2) vary during the simulation based on reactions of the redox species with oxygen or a user defined carbon source (modeled as a generic carbon compound). If the model is configured for varying redox couples, oxygen is also consumed by the carbon source or by oxidation of ferrous iron, sulfide, or methane. The user can enter a different first-order dechlorination rate for iron-dominated, sulfur-dominated, and methane-dominated redox conditions.

Table 36 lists the chemical species included in this reaction module. Figure 30 shows the conceptual model describing the degradation reactions modeled in this reaction module. Note that the carbon dioxide concentration is set to a constant value in the reaction module (because a buffered system is assumed). Thus, the methane-dominated redox condition is dependent only on variations in methane concentration. Ferric iron is modeled as an immobile species and all other species are mobile.

Table 36. *Chemical Species Included in the Redox-Linked Dechlorination of Chloroethenes Reaction Module*

No.	Abbreviation ^a	Chemical Name	Selected Alternate Name	CAS ^b Registry Number	Molecular Weight ^c (g/mol)	Chemical Formula
1	PCE	Tetrachloroethene	Tetrachloroethylene; Perchloroethylene	127-18-4	165.83340	C ₂ Cl ₄
2	TCE	Trichloroethene	Trichloroethylene	79-01-6	131.38834	C ₂ HCl ₃
3	cDCE	cis-1,2-Dichloroethene	cis-1,2-Dichloroethylene; cis-1,2-DCE; cis-DCE	156-59-2	96.94328	C ₂ H ₂ Cl ₂
4	tDCE	trans-1,2-Dichloroethene	trans-1,2-Dichloroethylene; trans-1,2-DCE; trans-DCE	156-60-5	96.94328	C ₂ H ₂ Cl ₂
5	11DCE	1,1-Dichloroethene	Vinylidene Chloride; 1,1-DCE	75-35-4	96.94328	C ₂ H ₂ Cl ₂
6	VC	Chloroethene	Vinyl Chloride	75-01-4	62.49822	C ₂ H ₃ Cl
7	OXY	Oxygen (dimer)	Dissolved Oxygen	7782-44-7	31.9988	O ₂
8	NIT	Nitrate anion	—	14797-55-8	62.0049	NO ₃ ⁻
9	FE2	Ferrous Iron cation	Iron (II)	15438-31-0	55.8450	Fe ²⁺
10	SO4	Sulfate anion	Sulphate	14808-79-8	96.0626	SO ₄ ²⁻
11	HS	Hydrosulfide	Bisulfide	15035-72-0	33.07294	HS ⁻
12	CH4	Methane	—	74-82-8	16.04246	CH ₄
13	DOC	Carbon Source ^d	Dissolved Organic Carbon	N/A	30.02598	CH ₂ O
14	Tracer	Conservative Tracer	—	N/A	N/A	N/A
15	FE3	Ferric Hydroxide (amorphous)	iron hydroxide; ferric iron; iron (III)	1309-33-7	106.86702	Fe(OH) ₃

^a These abbreviations refer to the specific chemicals listed here and should not be confused with different chemicals that may use the same abbreviation in other reaction modules.

^b CAS = Chemical Abstracts Service (see <http://www.cas.org/EO/regsys.html>)

^c Based on International Union of Pure and Applied Chemistry values reported by Loss [2003].

^d Dissolved organic carbon is represented by a simple hydrocarbon (based on the generic formula for an organic compound of C_nH_{2n}O_n with n=1). Concentration of actual dissolved organic carbon must be converted to this basis for this reaction module.

N/A – Not Applicable

	Contaminants	Contaminant Reaction	Dominant Redox Couple or Electron Acceptor	pE Range where the redox couple controls the dechlorination rate ^a	Redox Reactions (if varying redox conditions are being modelled)
Aerobic	cDCE, tDCE, 11DCE, VC	 First-Order Degradation ^b	O ₂	N/A	
		 NoDegradation (Inhibits Reactions Below)	NO ₃ ⁻	N/A	
Anoxic / Anaerobic	PCE, TCE,	 First-Order Dechlorination	Fe ²⁺ / Fe ³⁺ ^c	1.57 to - 3.42	
	cDCE, tDCE, 11DCE,	 First-Order Dechlorination	HS ⁻ / SO ₄ ²⁻	- 3.42 to - 3.89	
	VC	 First-Order Dechlorination	CH ₄ / CO ₂	< - 3.89	

^a Above the indicated pE range, the rates rapidly diminish to zero. The pE range was selected to represent when the reduction of the indicated electron acceptor is active.
^b Aerobic degradation results in mineralization of the contaminants (no daughter contaminants formed).
^c Fe³⁺ is modelled as amorphous ferric hydroxide to calculate the redox conditions.

Figure 30. Conceptual Model for the Dechlorination Reactions of the Redox-Linked Dechlorination of Chloroethenes Reaction Module

The conceptual model considers the rate of dechlorination or aerobic degradation as a function of the oxidation-reduction potential (at a fixed pH of 7) as controlled by key redox species that are commonly measured. These redox species also indicate the classes of microbial processes in the subsurface that are important for dechlorination or contaminant degradation reactions. The aerobic redox condition and associated degradation reactions are indicated sufficiently by the concentration of oxygen. When oxygen concentration is very low or oxygen is absent, anaerobic redox is divided into four different conditions. If nitrate is present at some location within the model domain, all other anaerobic reactions at that location are inhibited based on a user-specified inhibition coefficient. If nitrate is not present or has been depleted below the inhibitory level, anaerobic dechlorination can proceed at rates depending on the dominant electron acceptor process. The dominant electron acceptor process is defined by the relative concentrations of the redox couples shown in Figure 30. For iron, the redox potential is only a function of the ferrous iron concentration because ferric iron is only present as a solid. Ferric iron concentration are only important if the user desires to track changes in redox couples as impacted through oxidation by oxygen or through reduction by a carbon source. The sulfur redox potential is defined by the relative concentrations of sulfate and hydrosulfide (or dissolved sulfide converted to the equivalent hydrosulfide concentration based on the pH). The lowest possible redox potential occurs when methane is being produced. This redox couple uses a fixed dissolved CO₂ concentration in the reaction module such that the redox potential only varies as a function of the methane concentration. The module calculates the redox potential for each anaerobic redox

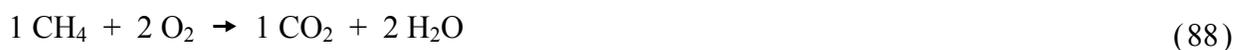
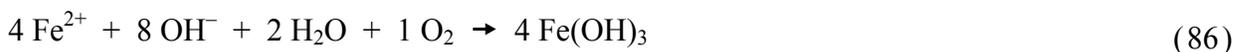
couple and the redox potential is set to the minimum value calculated for the three couples. Based on this minimum calculated redox potential, the module calculates dechlorination rates with the user-defined dechlorination rate coefficient associated with the redox range listed in Figure 30.

7.2 Reaction Equations

The basic functionality of this reaction module is described in this section for the 15 chemical species in Table 36. See Table 38 for a detailed itemization of all reaction parameters used in this reaction module.

The user must input a flag value to define the simulation as having static redox conditions or varying redox conditions. Static redox conditions may be useful if a user would like to interpolate available geochemical data and then let the module compute the distribution of related reaction rates. This rate distribution would then be used throughout the timeframe of the simulations. Use of static conditions may be suitable if it is unlikely that there will be significant changes in geochemical conditions over the duration of the simulation. By setting the flag to a value of "1" for static redox conditions, the reaction module computes the reaction rates in the first time step of the simulation based on the concentration distribution at the first time step (nominally the initial conditions). The module then holds these reaction rates constant throughout the simulation time period, though the rates will be spatially variable according to the input distribution of redox indicators. The module also sets the concentration of the redox indicators to zero after the first time step so that transport of these species is not tracked. By setting the flag to a value of "0" for varying redox conditions, the reaction module uses the full set of reactions described below at each time step to determine the dechlorination rates and associated concentration changes for each time step in the simulation.

If oxygen is present, the module first uses instantaneous (equilibrium) stoichiometric reactions (Equations 85 to 88) to deplete oxygen by sequential reaction with dissolved DOC, FE2, HS, and/or CH4 to the point where either all oxygen is consumed or all of these compounds are consumed. The initial concentrations (denoted as [Species]) for DOC, FE2, HS, CH4, and OXY are reduced to the post-oxidation concentrations [Species]_{ox}, which are used in the subsequent pE and dechlorination rate calculations.



The initial oxygen concentration (prior to any oxidation reactions) inhibits anaerobic dechlorination reactions, as does the nitrate concentration (Equations 89 and 90). Oxygen must be present after the oxidation reactions for aerobic degradation of DCE isomers and VC to occur, which is enforced using the Monod term in Equation 91. However, the module does not consider consumption of oxygen during DCE isomer or VC oxidation.

$$OxyInhib = \left(\frac{k_{io}}{k_{io} + [OXY]} \right) \quad (89)$$

$$NitInhib = \left(\frac{k_{in}}{k_{in} + [NIT]} \right) \quad (90)$$

$$OxyPromo = \left(\frac{[OXY]_{ox}}{K_{O_2} + [OXY]_{ox}} \right) \quad (91)$$

If the initial oxygen concentration is greater than 0.1 mg/L, then reduction of electron acceptors is not allowed in the same transport time step where they just underwent oxidization (i.e., rates of electron acceptor reduction are set to zero). If the initial oxygen concentration in a transport time step is less than 0.1 mg/L, then electron acceptors will undergo reduction at a rate depending on the electron acceptor and DOC concentration and inhibited by the initial oxygen concentration. Electron acceptors are sequentially inhibited based on 10% of the Monod half-saturation coefficient for nitrate and the Monod half-saturation coefficients for iron and sulfate. The DOC Monod half-saturation coefficient is defined as 1.0 E-4 mol/L for nitrate, iron, and sulfate and as 1.0 E-5 mol/L for methane. Equations 92 through 95 define the rates of electron acceptor reduction when the initial oxygen concentration is less than 0.1 mg/L.

$$r_{NIT} = k_{NIT} \cdot \left(\frac{[NIT]}{K_n + [NIT]} \right) \cdot \left(\frac{[DOC]_{ox}}{10^{-4} + [DOC]_{ox}} \right) \cdot OxyInhib \quad (92)$$

$$r_{FE3} = k_{FE3} \cdot \left(\frac{[FE3]_{ox}}{K_f + [FE3]_{ox}} \right) \cdot \left(\frac{[DOC]_{ox}}{10^{-4} + [DOC]_{ox}} \right) \cdot OxyInhib \cdot \left(\frac{0.1 \cdot K_n}{0.1 \cdot K_n + [NIT]} \right) \quad (93)$$

$$r_{SO4} = k_{SO4} \cdot \left(\frac{[SO4]_{ox}}{K_s + [SO4]_{ox}} \right) \cdot \left(\frac{[DOC]_{ox}}{10^{-4} + [DOC]_{ox}} \right) \cdot OxyInhib \cdot \left(\frac{0.1 \cdot K_n}{0.1 \cdot K_n + [NIT]} \right) \cdot \left(\frac{K_f}{K_f + [FE3]_{ox}} \right) \quad (94)$$

$$r_{CH4} = \mu_{CH4} \cdot \left(\frac{[DOC]_{ox}}{10^{-5} + [DOC]_{ox}} \right) \cdot OxyInhib \cdot \left(\frac{0.1 \cdot K_n}{0.1 \cdot K_n + [NIT]} \right) \cdot \left(\frac{K_f}{K_f + [FE3]_{ox}} \right) \cdot \left(\frac{K_s}{K_s + [SO4]_{ox}} \right) \quad (95)$$

Three redox couples are represented in this reaction module:

1. Fe iron (ferrous iron / amorphous ferric hydroxide)
2. S sulfur (sulfate / hydrosulfide)
3. C methane (methane / CO₂)

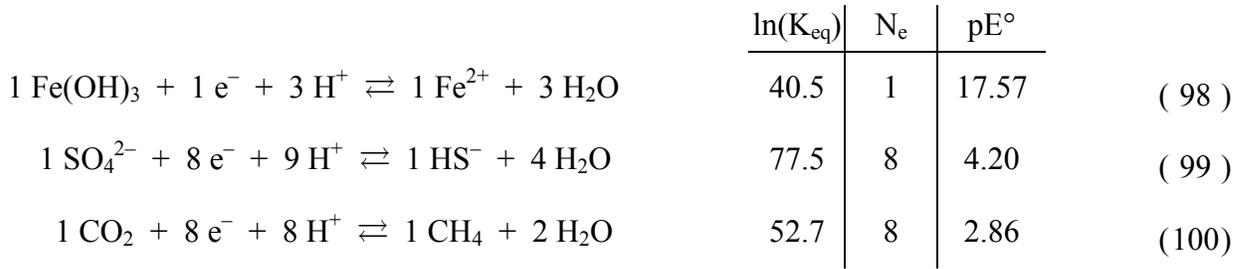
The redox potential (pE) of a redox couple is calculated from the Nernst equation (Equation 96) using the number of electrons transferred (N_e) and the product of the reactant species concentrations to the power of the respective stoichiometric coefficients (b_i) divided by the product of the product species concentrations to the power of the respective stoichiometric coefficients (b_j) [Drever, 1988]. Assuming dilute aqueous solution, species concentrations are used in place of chemical activities. For solid species (e.g., Fe(OH)₃), the chemical activity is taken as 1.0. Equation 97 [Drever, 1988] is used to calculate the pE° at standard conditions (298.15 K, 1 atm, and unit activity) based on tabulated values of ΔG° (R is the gas constant, equal to 8.314472 J·K⁻¹·mol⁻¹). Free energies for the species important to the three redox couples of interest are given in Table 37. The reactions for these three redox couples are listed in Equations 98 to 100 along with calculated values for the terms of the pE° equation. The pE for each anaerobic redox couple is thus calculated for a pH of 7 (i.e., [H⁺] = 10⁻⁷ mol/L) using Equations 101 to 103 (substituting in pE° values). These equations assume that the system is well buffered, thus the pH is constant and the concentration of CO₂ is constant at a value of 0.001 mol/L. At a very low concentration of a reduced species (FE₂, HS, or CH₄), the pE is set to an arbitrarily high value of 8.0 to prevent numerical problems. To avoid dealing with negative pE numbers in this reaction module, the pE values are shifted upwards by 10 units to obtain pE' (i.e., pE' = pE + 10). The dominant redox couple is determined as the minimum of these three pE' values (Equation 104).

$$pE = pE^\circ + \frac{1}{N_e} \cdot \text{Log}_{10} \left(\frac{\prod_{i=1}^{\# \text{ reactants}} [\text{reactant}_i]^{b_i}}{\prod_{j=1}^{\# \text{ products}} [\text{product}_j]^{b_j}} \right) \quad (96)$$

$$pE^\circ = \frac{1}{N_e} \cdot \text{Log}_{10}(K_{eq}) = \frac{1}{N_e} \cdot \text{Log}_{10} \left(\frac{-\Delta G^\circ}{R \cdot T} \right) = \frac{1}{N_e} \cdot \frac{\text{Log}_e \left(\frac{-\Delta G^\circ}{R \cdot T} \right)}{\text{Log}_e(10)} \quad (97)$$

Table 37. Free Energy for Chemical Species of Interest [Drever, 1988]

Chemical Species	ΔG° (kJ)
H ₂ O	-237.13
Fe(OH) ₃	-696.5
Fe ²⁺	-85.35
SO ₄ ²⁻	-744.53
HS ⁻	12.08
CO ₂	-394.36
CH ₄	-50.72



$$pE_F = 17.57 + \text{Log}_{10} \left(\frac{10^{-21}}{[FE2]_{ox}} \right) \quad (\text{for } FE2 > 10^{-7} \text{ mol/L; } pE_F \equiv 8.0 \text{ otherwise}) \quad (101)$$

$$pE_S = 4.20 + \left(\frac{1}{8} \right) \cdot \text{Log}_{10} \left(\frac{[SO4]_{ox} \cdot 10^{-63}}{[HS]_{ox}} \right) \quad (\text{for } HS > 10^{-7} \text{ mol/L; } pE_S \equiv 8.0 \text{ otherwise}) \quad (102)$$

$$pE_C = 2.86 + \left(\frac{1}{8} \right) \cdot \text{Log}_{10} \left(\frac{[CO2] \cdot 10^{-56}}{[CH4]_{ox}} \right) \quad (\text{for } CH4 > 10^{-7} \text{ mol/L; } pE_C \equiv 8.0 \text{ otherwise}) \quad (103)$$

$$pE'_{\text{dominant}} = \text{Minimum}(pE'_F, pE'_S, pE'_C) \quad (104)$$

As the pE' value for an aqueous solution decreases, the redox conditions are controlled by the iron, sulfur, and methane couples beginning at pE' values of 11.57, 6.58, and 6.11, respectively. Based on the dominant redox couple (i.e., pE'_{dominant}), fractional activities (pctFe, pctS, and pctC for iron, sulfur, and methane, respectively) are determined for each redox couple from the curves shown in Figure 31. "Fractional activities" (not to be confused with chemical activity) are assigned as values from 0.0 to 1.0 and are multipliers on the reaction rates (as discussed below). For a fractional activity of 1.0, the regime is fully active. When multiple regimes are active, only the leftmost regime on the pE' scale is allowed to impact the dechlorination rates (except in

transition zones, which are small). A sigmoidal function is used to provide a smooth (albeit steep) transition at the control points instead of using a step function (i.e., if/then logic). Sigmoidal function parameters (steepness and inflection point) were selected based on a 0.1 pE' unit change (i.e., the transition zone) where the fractional activity value changes from 0.0 to 1.0.

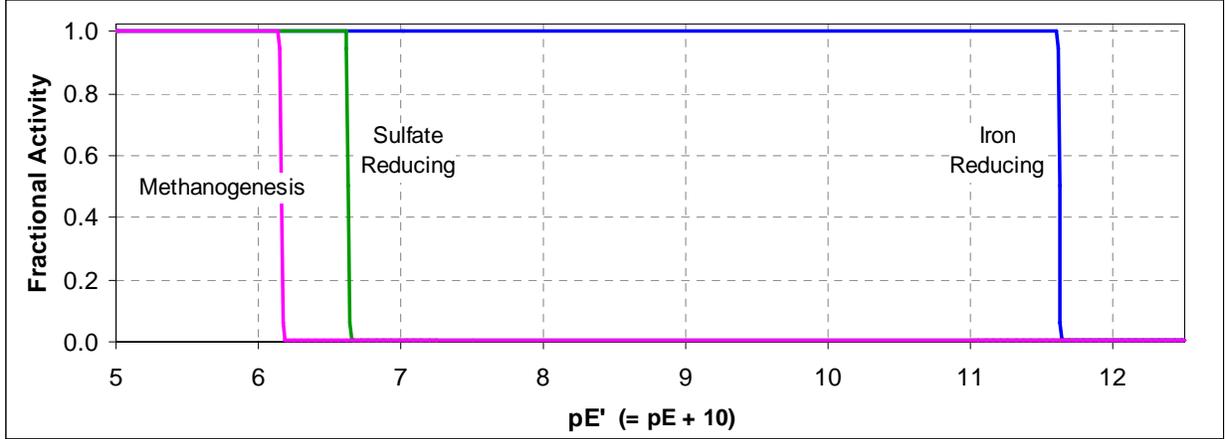


Figure 31. *pE Value (On a Shifted Scale) at Which Each Anaerobic Dechlorination Mechanism Dominates*

Anaerobic dechlorination rates are calculated based on the contaminant concentration, the inhibition from oxygen and nitrate, and the user-defined dechlorination rate coefficient associated with the dominant redox couple. Equations 105 to 110 describe the anaerobic dechlorination rates. These equations are implemented such that the dechlorination rates for only one redox regime apply (except in the small transition zone windows, where multiple regimes may apply at less than full activity). For example, at a pE'_{dominant} value of 6.5, the fractional activities from Figure 31 for iron, sulfur, and methane, respectively, are 1.0, 1.0, and 0.0. The dechlorination rate in this example is that for sulfate ($kan_{Fe} + kan_S - kan_{Fe} + 0.0 = kan_S$)

$$ran_{PCE} = [PCE] \cdot OxyInhib \cdot NitInhib \cdot (kan_{PCE_{Fe}} \cdot pctFe + (kan_{PCE_S} - kan_{PCE_{Fe}}) \cdot pctS + (kan_{PCE_C} - kan_{PCE_S}) \cdot pctC) \quad (105)$$

$$ran_{TCE} = [TCE] \cdot OxyInhib \cdot NitInhib \cdot (kan_{TCE_{Fe}} \cdot pctFe + (kan_{TCE_S} - kan_{TCE_{Fe}}) \cdot pctS + (kan_{TCE_C} - kan_{TCE_S}) \cdot pctC) \quad (106)$$

$$ran_{cDCE} = [cDCE] \cdot OxyInhib \cdot NitInhib \cdot (kan_{cDCE_{Fe}} \cdot pctFe + (kan_{cDCE_S} - kan_{cDCE_{Fe}}) \cdot pctS + (kan_{cDCE_C} - kan_{cDCE_S}) \cdot pctC) \quad (107)$$

$$ran_{tDCE} = [tDCE] \cdot OxyInhib \cdot NitInhib \cdot (kan_{tDCE_{Fe}} \cdot pctFe + (kan_{tDCE_S} - kan_{tDCE_{Fe}}) \cdot pctS + (kan_{tDCE_C} - kan_{tDCE_S}) \cdot pctC) \quad (108)$$

$$\begin{aligned} \text{ran}_{11\text{DCE}} = & [\text{11DCE}] \cdot \text{OxyInhib} \cdot \text{NitInhib} \\ & \cdot \left(\text{kan}_{11\text{DCE_Fe}} \cdot \text{pctFe} + (\text{kan}_{11\text{DCE_S}} - \text{kan}_{11\text{DCE_Fe}}) \cdot \text{pctS} + (\text{kan}_{11\text{DCE_C}} - \text{kan}_{11\text{DCE_S}}) \cdot \text{pctC} \right) \end{aligned} \quad (109)$$

$$\begin{aligned} \text{ran}_{\text{VC}} = & [\text{VC}] \cdot \text{OxyInhib} \cdot \text{NitInhib} \\ & \cdot \left(\text{kan}_{\text{VC_Fe}} \cdot \text{pctFe} + (\text{kan}_{\text{VC_S}} - \text{kan}_{\text{VC_Fe}}) \cdot \text{pctS} + (\text{kan}_{\text{VC_C}} - \text{kan}_{\text{VC_S}}) \cdot \text{pctC} \right) \end{aligned} \quad (110)$$

The set of differential equations describing the reaction kinetics for all species is given in Equations 111 through 125.

$$\frac{d[\text{PCE}]}{dt} = -\text{ran}_{\text{PCE}} \quad (111)$$

$$\frac{d[\text{TCE}]}{dt} = -\text{ran}_{\text{TCE}} + \text{ran}_{\text{PCE}} \quad (112)$$

$$\frac{d[\text{cDCE}]}{dt} = -\text{ran}_{\text{cDCE}} + \text{ran}_{\text{TCE}} \cdot F_{\text{cDCE/TCE}} - \text{kae}_{\text{cDCE}} \cdot \text{OxyPromo} \cdot [\text{cDCE}] \quad (113)$$

$$\frac{d[\text{tDCE}]}{dt} = -\text{ran}_{\text{tDCE}} + \text{ran}_{\text{TCE}} \cdot F_{\text{tDCE/TCE}} - \text{kae}_{\text{tDCE}} \cdot \text{OxyPromo} \cdot [\text{tDCE}] \quad (114)$$

$$\frac{d[\text{11DCE}]}{dt} = -\text{ran}_{\text{11DCE}} + \text{ran}_{\text{TCE}} \cdot F_{\text{11DCE/TCE}} - \text{kae}_{\text{11DCE}} \cdot \text{OxyPromo} \cdot [\text{11DCE}] \quad (115)$$

$$\frac{d[\text{VC}]}{dt} = -\text{ran}_{\text{VC}} + \text{ran}_{\text{cDCE}} \cdot F_{\text{VC/cDCE}} + \text{ran}_{\text{tDCE}} \cdot F_{\text{VC/tDCE}} + \text{ran}_{\text{11DCE}} \cdot F_{\text{VC/11DCE}} - \text{kae}_{\text{VC}} \cdot \text{OxyPromo} \cdot [\text{VC}] \quad (116)$$

$$\frac{d[\text{OXY}]}{dt} = 0.0 \quad \text{(Oxygen is consumed by equilibrium oxidation reactions, but kinetic consumption of oxygen during DCE or VC biodegradation is not tracked because those are modeled as first-order processes.)} \quad (117)$$

$$\frac{d[\text{NIT}]}{dt} = -r_{\text{NIT}} \cdot [\text{NIT}] \quad (118)$$

$$\frac{d[\text{FE2}]}{dt} = r_{\text{FE3}} \cdot [\text{FE3}]_{\text{ox}} \quad (119)$$

$$\frac{d[\text{SO4}]}{dt} = -r_{\text{SO4}} \cdot [\text{SO4}]_{\text{ox}} \quad (120)$$

$$\frac{d[\text{HS}]}{dt} = r_{\text{SO4}} \cdot [\text{SO4}]_{\text{ox}} \quad (121)$$

$$\frac{d[CH_4]}{dt} = r_{CH_4} \quad (122)$$

$$\frac{d[DOC]}{dt} = -r_{NIT} \cdot F_{DOC/NIT} \cdot [NIT]_{ox} - r_{FE3} \cdot F_{DOC/FE3} \cdot [FE3]_{ox} - r_{SO_4} \cdot F_{DOC/SO_4} \cdot [SO_4]_{ox} \quad (123)$$

$$\frac{d[Tracer]}{dt} = 0.0 \quad (\text{Conservative [non-reactive] tracer.}) \quad (124)$$

$$\frac{d[FE3]}{dt} = -r_{FE3} \cdot [FE3]_{ox} \quad (125)$$

7.3 Required Input

The reaction parameters for this reaction module are made available to RT3D as part of the input for the Reaction Package. The Reaction Package input file structure is discussed in the RT3D manual and addendum [Clement, 1997; Clement and Johnson, 2002]. The 39 reaction parameters that must be specified for this reaction module are listed in Table 38 in the required order (ID Number) with units and a description. Site-specific knowledge from field data or laboratory tests should be applied to determine an appropriate model configuration for reaction parameters (i.e., the values and the spatial distribution).

Table 38. *Input Parameters for the Redox-Linked Dechlorination of Chloroethenes Reaction Module*

ID #	Parameter	Fortran Variable	Units	Description
1	IsStatic	IsStatic	--	Value to signify whether the redox-dependant dechlorination rates are to be held constant (static) after an initial determination (1) or if the spatial distribution of redox conditions will be allowed to vary over time (0).
2	$F_{cDCE/TCE}$	f_cdce_tce	mol/mol	Molar stoichiometry of conversion from TCE to cDCE (based on site specific observation)
3	$F_{tDCE/TCE}$	f_tdce_tce	mol/mol	Molar stoichiometry of conversion from TCE to tDCE (based on site specific observation)
4	$F_{11DCE/TCE}$	f_11dce_tce	mol/mol	Molar stoichiometry of conversion from TCE to 11DCE (based on site specific observation)
5	$F_{VC/cDCE}$	f_vc_cdce	mol/mol	Molar stoichiometry of conversion from cDCE to VC (based on site specific observation)
6	$F_{VC/tDCE}$	f_vc_tdce	mol/mol	Molar stoichiometry of conversion from tDCE to VC (based on site specific observation)

Table 38. (contd)

ID #	Parameter	Fortran Variable	Units	Description
7	$F_{VC/11DCE}$	f_vc_11dce	mol/mol	Molar stoichiometry of conversion from 11DCE to VC (based on site specific observation)
8	K_{O_2}	Ko2	mg/L	Monod half-saturation coefficient for oxygen as part of aerobic dechlorination reactions
9	K_n	Kn	mg/L	Monod half-saturation coefficient for nitrate reduction
10	K_f	Kf	mg/L	Monod half-saturation coefficient for iron reduction
11	K_s	Ks	mg/L	Monod half-saturation coefficient for sulfate reduction
12	k_{io}	kio	mg/L	Inhibition coefficient for oxygen on anaerobic activity
13	k_{in}	kin	mg/L	Inhibition coefficient for nitrate on anaerobic activity
14	kan_{PCE_Fe}	kan_pce_Fe	1/day	First-order decay coefficient for anaerobic dechlorination of PCE under iron dominated redox potential
15	kan_{PCE_S}	kan_pce_S	1/day	First-order decay coefficient for anaerobic dechlorination of PCE under sulfur dominated redox potential
16	kan_{PCE_C}	kan_pce_C	1/day	First-order decay coefficient for anaerobic dechlorination of PCE under methane dominated redox potential
17	kan_{TCE_Fe}	kan_tce_Fe	1/day	First-order decay coefficient for anaerobic dechlorination of TCE under iron dominated redox potential
18	kan_{TCE_S}	kan_tce_S	1/day	First-order decay coefficient for anaerobic dechlorination of TCE under sulfur dominated redox potential
19	kan_{TCE_C}	kan_tce_C	1/day	First-order decay coefficient for anaerobic dechlorination of TCE under methane dominated redox potential
20	kan_{cDCE_Fe}	kan_cdce_Fe	1/day	First-order decay coefficient for anaerobic dechlorination of cDCE under iron dominated redox potential
21	kan_{cDCE_S}	kan_cdce_S	1/day	First-order decay coefficient for anaerobic dechlorination of cDCE under sulfur dominated redox potential
22	kan_{cDCE_C}	kan_cdce_C	1/day	First-order decay coefficient for anaerobic dechlorination of cDCE under methane dominated redox potential
23	kan_{tDCE_Fe}	kan_tdce_Fe	1/day	First-order decay coefficient for anaerobic dechlorination of tDCE under iron dominated redox potential
24	kan_{tDCE_S}	kan_tdce_S	1/day	First-order decay coefficient for anaerobic dechlorination of tDCE under sulfur dominated redox potential
25	kan_{tDCE_C}	kan_tdce_C	1/day	First-order decay coefficient for anaerobic dechlorination of tDCE under methane dominated redox potential
26	kan_{11DCE_Fe}	kan_11dce_Fe	1/day	First-order decay coefficient for anaerobic dechlorination of 11DCE under iron dominated redox potential
27	kan_{11DCE_S}	kan_11dce_S	1/day	First-order decay coefficient for anaerobic dechlorination of 11DCE under sulfur dominated redox potential

Table 38. (contd)

ID #	Parameter	Fortran Variable	Units	Description
28	$k_{an_{11DCE_C}}$	kan_11dce_C	1/day	First-order decay coefficient for anaerobic dechlorination of 11DCE under methane dominated redox potential
29	$k_{an_{VC_Fe}}$	kan_vc_Fe	1/day	First-order decay coefficient for anaerobic dechlorination of VC under iron dominated redox potential
30	$k_{an_{VC_S}}$	kan_vc_S	1/day	First-order decay coefficient for anaerobic dechlorination of VC under sulfur dominated redox potential
31	$k_{an_{VC_C}}$	kan_vc_C	1/day	First-order decay coefficient for anaerobic dechlorination of VC under methane dominated redox potential
32	$k_{ae_{cDCE}}$	kae_cdce	1/day	First-order decay coefficient for aerobic dechlorination of cis-1,2-DCE
33	$k_{ae_{tDCE}}$	kae_tdce	1/day	First-order decay coefficient for aerobic dechlorination of trans-1,2-DCE
34	$k_{ae_{11DCE}}$	kae_11dce	1/day	First-order decay coefficient for aerobic dechlorination of 1,1-DCE
35	$k_{ae_{VC}}$	kae_vc	1/day	First-order decay coefficient for aerobic dechlorination of VC
36	k_{NIT}	kNit	1/day	Maximum rate of nitrate reduction
37	k_{FE3}	kFe3	1/day	Maximum rate of iron reduction
38	k_{SO4}	kSO4	1/day	Maximum rate of sulfate reduction
39	μ_{CH4}	uCH4	mg/day	Maximum rate of methane production

7.4 Example Simulations

Simulations with this reaction module were conducted with RT3D in a batch reactor (no flow) mode to show examples of how the reaction module simulates the pattern of dechlorination. The parameter values for each example simulation are listed in Tables 39 and 40. These parameters are arbitrary values and are not directly related to any specific laboratory data. Site-specific values would need to be determined as part of a calibration process. Results for these example batch simulations are shown in the Figures 32 through 35, respectively.

Table 39. Parameter Values for Example Simulations 1 and 2 with the Redox-Linked Dechlorination of Chloroethenes Reaction Module

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	IsStatic	0	--	21	kan_cdce_S	0.0045	1/day
2	f_cdce_tce	1	mol/mol	22	kan_cdce_C	0.005	1/day
3	f_tdce_tce	0	mol/mol	23	kan_tdce_Fe	0	1/day
4	f_11dce_tce	0	mol/mol	24	kan_tdce_S	0	1/day
5	f_vc_cdce	1	mol/mol	25	kan_tdce_C	0	1/day
6	f_vc_tdce	1	mol/mol	26	kan_11dce_Fe	0	1/day
7	f_vc_11dce	1	mol/mol	27	kan_11dce_S	0	1/day
8	Ko2	0.5	mg/L	28	kan_11dce_C	0	1/day
9	Kn	0.5	mg/L	29	kan_vc_Fe	0.001	1/day
10	Kf	0.05	mg/L	30	kan_vc_S	0.0005	1/day
11	Ks	0.1	mg/L	31	kan_vc_C	0.0005	1/day
12	kio	0.1	mg/L	32	kae_cdce	0.01	1/day
13	kin	1	mg/L	33	kae_tdce	0	1/day
14	kan_pce_Fe	0.0005	1/day	34	kae_11dce	0	1/day
15	kan_pce_S	0.001	1/day	35	kae_vc	0.01	1/day
16	kan_pce_C	0.005	1/day	36	kNit	0	1/day
17	kan_tce_Fe	0.001	1/day	37	kFe3	0	1/day
18	kan_tce_S	0.001	1/day	38	kSO4	0	1/day
19	kan_tce_C	0.004	1/day	39	uCH4	0	mg/day
20	kan_cdce_Fe	0.004	1/day				

Table 40. Parameter Values for Example Simulations 3 and 4 with the Redox-Linked Dechlorination of Chloroethenes Reaction Module

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	IsStatic	0	--	21	kan_cdce_S	0.0045	1/day
2	f_cdce_tce	1	mol/mol	22	kan_cdce_C	0.005	1/day
3	f_tdce_tce	0	mol/mol	23	kan_tdce_Fe	0	1/day
4	f_11dce_tce	0	mol/mol	24	kan_tdce_S	0	1/day
5	f_vc_cdce	1	mol/mol	25	kan_tdce_C	0	1/day
6	f_vc_tdce	1	mol/mol	26	kan_11dce_Fe	0	1/day
7	f_vc_11dce	1	mol/mol	27	kan_11dce_S	0	1/day
8	Ko2	0.5	mg/L	28	kan_11dce_C	0	1/day
9	Kn	0.5	mg/L	29	kan_vc_Fe	0.001	1/day
10	Kf	0.05	mg/L	30	kan_vc_S	0.0005	1/day
11	Ks	0.1	mg/L	31	kan_vc_C	0.0005	1/day
12	kio	0.1	mg/L	32	kae_cdce	0.01	1/day
13	kin	1	mg/L	33	kae_tdce	0	1/day
14	kan_pce_Fe	0.0005	1/day	34	kae_11dce	0	1/day
15	kan_pce_S	0.001	1/day	35	kae_vc	0.01	1/day
16	kan_pce_C	0.005	1/day	36	kNit	0.1	1/day
17	kan_tce_Fe	0.001	1/day	37	kFe3	0.1	1/day
18	kan_tce_S	0.001	1/day	38	kSO4	0.1	1/day
19	kan_tce_C	0.004	1/day	39	uCH4	0.1	mg/day
20	kan_cdce_Fe	0.004	1/day				

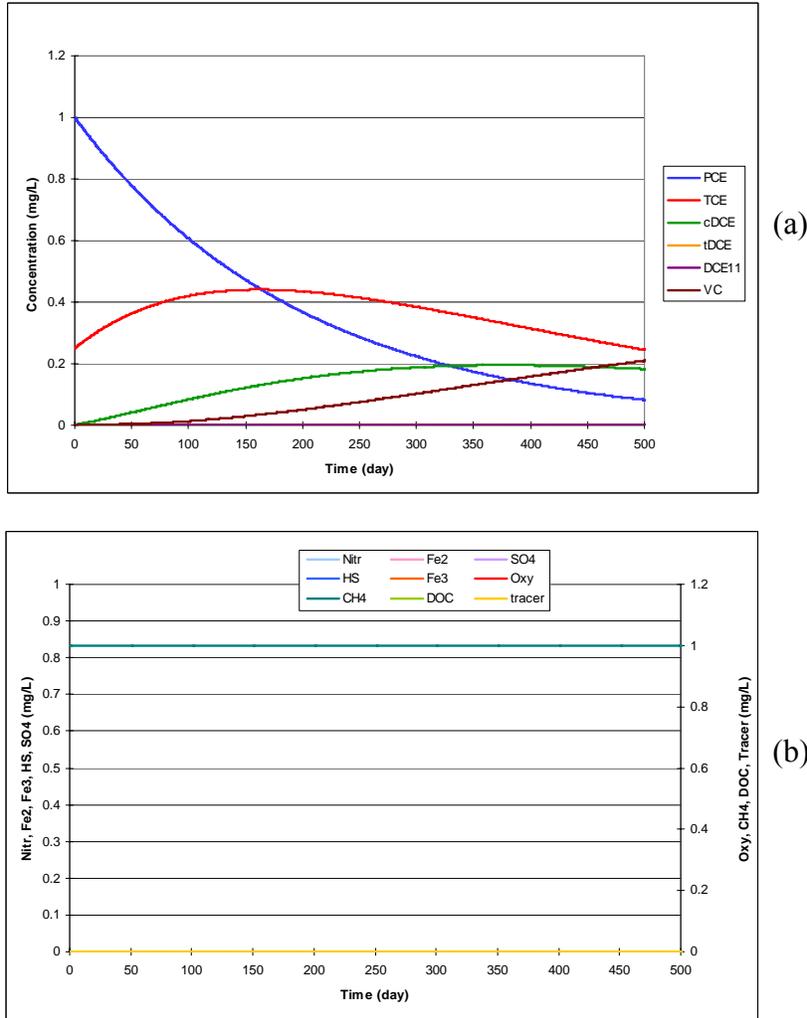


Figure 32. Example Simulation 1: Dechlorination of PCE and TCE Using the Parameter Values Shown in Table 39 — The initial concentration for PCE, TCE, and methane were 1, 0.25, and 1 mg/L, respectively. All other species concentrations started at zero. Note that the concentrations of redox species remain constant in this simulation. Figure (a) shows chlorinated solvent concentration. Figure (b) shows the concentration of other species.

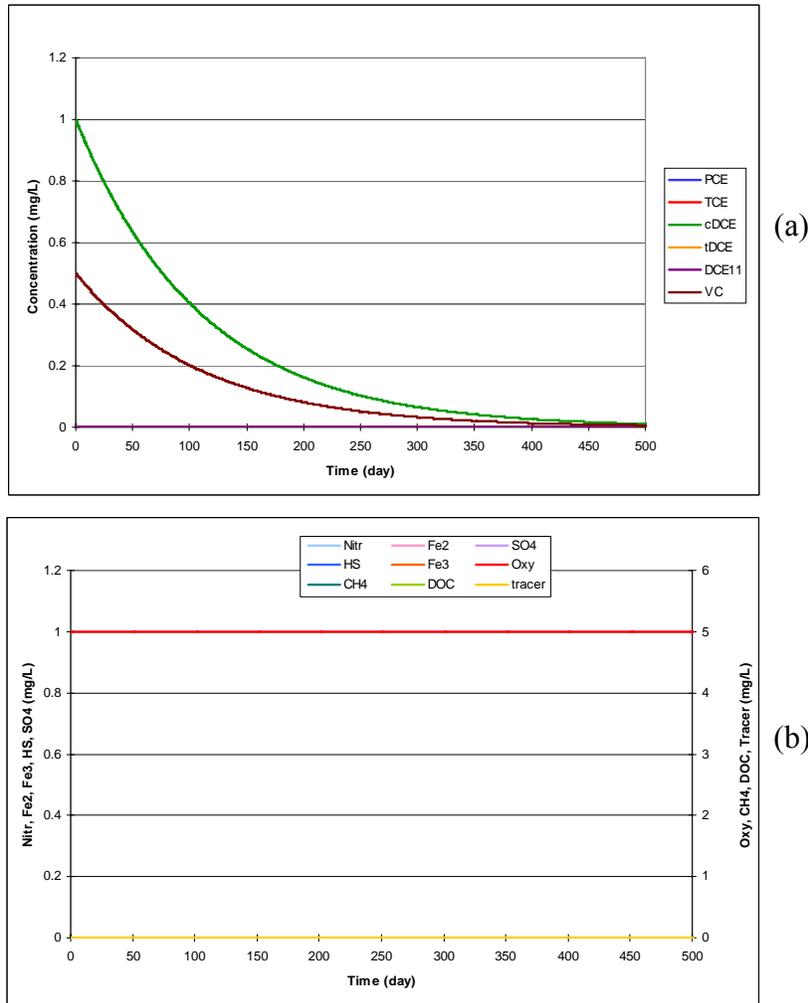


Figure 33. Example Simulation 2: Dechlorination of cDCE and VC Using the Parameter Values Shown in Table 39 — The initial concentration for cDCE, VC, oxygen, and nitrate were 1, 0.5, 5, and 1 mg/L, respectively. All other species concentrations started at zero. Note that the concentrations of redox species remain constant in this simulation. Figure (a) shows chlorinated solvent concentration. Figure (b) shows the concentration of other species.

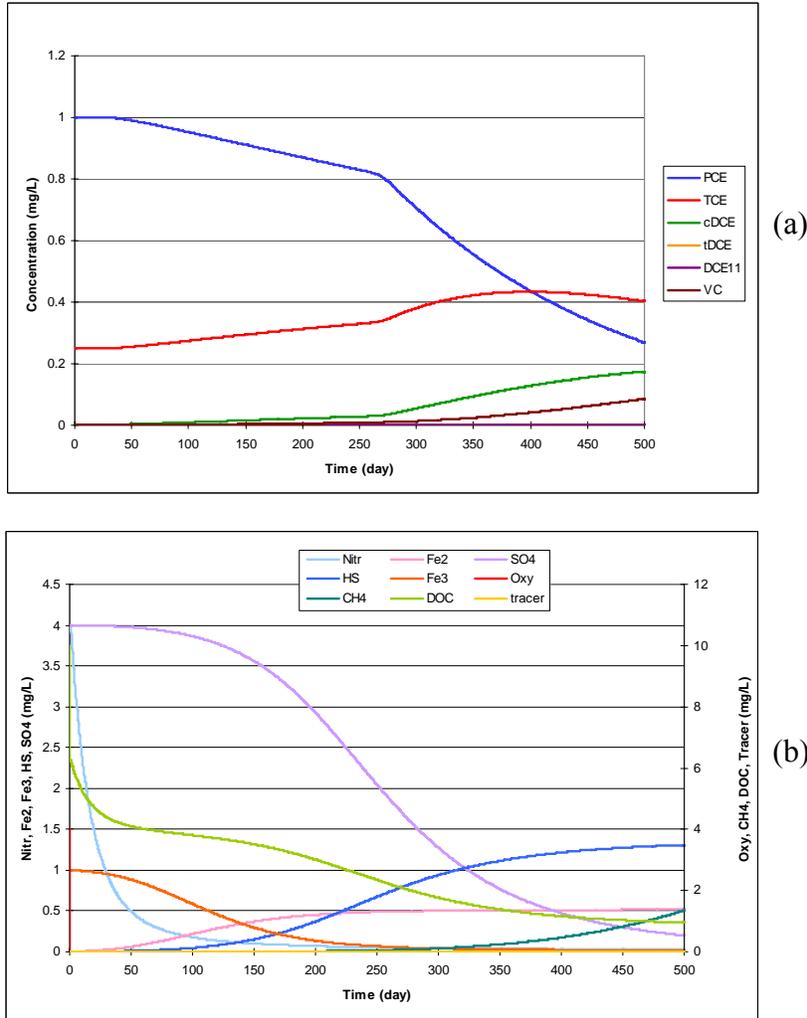


Figure 34. Example Simulation 3: Dechlorination of PCE and TCE Using the Parameter Values Shown in Table 40 — The initial concentration for PCE, TCE, oxygen, nitrate, sulfate, dissolved organic carbon, and iron(III) were 1, 0.25, 4, 4, 4, 10, and 1 mg/L, respectively. All other species concentrations started at zero. Note that the concentrations of redox species vary in this simulation according to oxidation processes and the reduction rate input parameters. Figure (a) shows chlorinated solvent concentration. Figure (b) shows the concentration of other species.

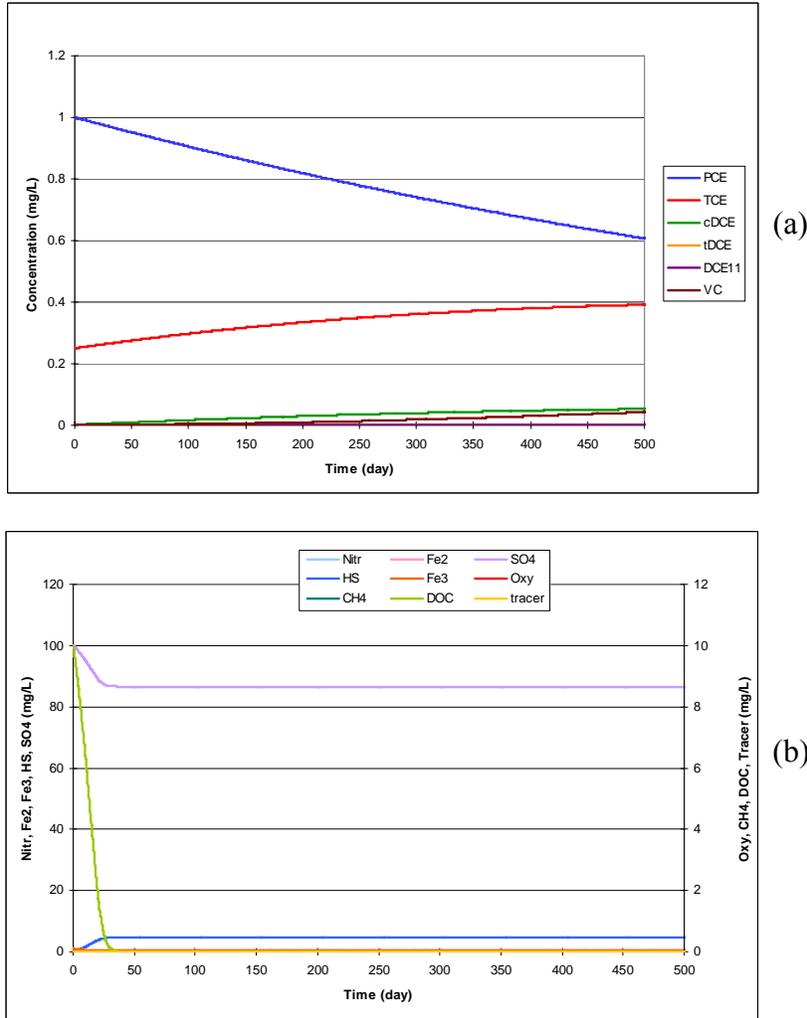


Figure 35. Example Simulation 4: Dechlorination of PCE and TCE Using the Parameter Values Shown in Table 40 — The initial concentration for PCE, TCE, sulfate, dissolved organic carbon, and iron(III) were 1, 0.25, 100, 10, and 1 mg/L, respectively. All other species concentrations started at zero. Note that the concentrations of redox species vary in this simulation according to oxidation processes and the reduction rate input parameters. Figure (a) shows chlorinated solvent concentration. Figure (b) shows the concentration of other species.

8.0 Substrate-Linked Reductive Dechlorination of Chloroethenes

8.1 Conceptual Model for Dechlorination Reactions

This reaction module describes reductive dechlorination of chlorinated ethene compounds linked to substrate metabolism (biostimulation) and corresponding biomass activity. The module includes an explicit description of biomass growth in response to consumption of lactate, propionate, acetate, hydrogen, and/or decaying biomass and separately models the metabolic activity of methanogens and other anaerobes able to metabolize lactate fermentation products. Both types of biomass will decay over time according to a user-specified decay rate. This reaction module does not account for changes in porosity/permeability resulting from biomass growth, although the total biomass is also tracked so that the modeler can assess the potential for biological fouling of the aquifer. If required, macroscopic models for biomass-affected porous media properties [Clement et al., 1996] could be combined with this module as a user-defined reaction module to account for changes in porosity/permeability. All anaerobic activity is inhibited by oxygen. Oxygen is depleted by lactate, propionate, or acetate through a stoichiometric reaction. Biomass growth is modeled with a Monod kinetic form, is dependent on substrate concentration, and is inhibited by high concentrations of organic acids. Reductive dechlorination of chlorinated ethene compounds is dependent on the concentration of the chlorinated ethene compound and methanogen biomass, and is inhibited by presence of higher-chlorinated ethene compounds (e.g., TCE inhibits the DCE dechlorination rate). Aerobic degradation of DCE and VC are modeled as first-order reactions (see the conceptual model description of the Mixed Chloroethene/ Chloroethane/Chloromethane Dechlorination reaction module for discussion on the assumption of first-order reaction kinetics).

The linkage of dechlorination to methanogenesis, similar to Skeen et al. [1995], is intended to provide a simplified conceptual model representing dechlorinating activity under methanogenic redox conditions, as an alternative to a detailed representation of all reaction mechanisms that may be involved.

Table 41 lists the chemical species included in this reaction module. Figure 36 shows the conceptual model describing the degradation reactions modeled in this reaction module.

Table 41. Chemical Species Included in the Substrate-Linked Reductive Dechlorination of Chloroethenes Reaction Module

No.	Abbreviation ^a	Chemical Name	Selected Alternate Name	CAS ^b Registry Number	Molecular Weight ^c (g/mol)	Chemical Formula
1	LAC	Lactate	2-hydroxy-propanoic acid (ion)	113-21-3 (lactic acid: 50-21-5)	89.0700	C ₃ H ₅ O ₃ ⁻
2	PRO	Propionate	Propanoic acid (ion)	72-03-7 (propionic acid: 79-09-4)	73.0706	C ₃ H ₅ O ₂ ⁻
3	ACE	Acetate	Acetic acid (ion)	71-50-1 (acetic acid: 64-19-7)	59.04402	C ₂ H ₃ O ₂ ⁻
4	H2	Hydrogen	—	1333-74-0	2.01588	H ₂
5	MET	Methane	—	74-82-8	16.04246	CH ₄
6	PCE	Tetrachloroethene	Perchloroethylene	127-18-4	165.83340	C ₂ Cl ₄
7	TCE	Trichloroethene	Trichloroethylene	79-01-6	131.38834	C ₂ HCl ₃
8	DCE	Dichloroethene (all isomers)	Dichloroethylene	156-59-2	96.94328	C ₂ H ₂ Cl ₂
9	VC	Chloroethene	Vinyl Chloride	75-01-4	62.49822	C ₂ H ₃ Cl
10	ETH	Ethene	ethylene	74-85-1	28.05316	C ₂ H ₄
11	OXY	Oxygen (dimer)	dissolved oxygen	7782-44-7	31.9988	O ₂
12	Tracer	Conservative Tracer	—	N/A	N/A	N/A
13	Bio1	Fermentors	—	N/A	113.11458	C ₅ H ₇ O ₂ N
14	Bio2	Methanogens	—	N/A	113.11458	C ₅ H ₇ O ₂ N
15	BioT	Total Biomass	—	N/A	113.11458	C ₅ H ₇ O ₂ N

^a These abbreviations refer to the specific chemicals listed here and should not be confused with different chemicals that may use the same abbreviation in other reaction modules.

^b CAS = Chemical Abstracts Service (see <http://www.cas.org/EO/regsys.html>)

^c Based on International Union of Pure and Applied Chemistry values reported by Loss [2003].

N/A – Not Applicable

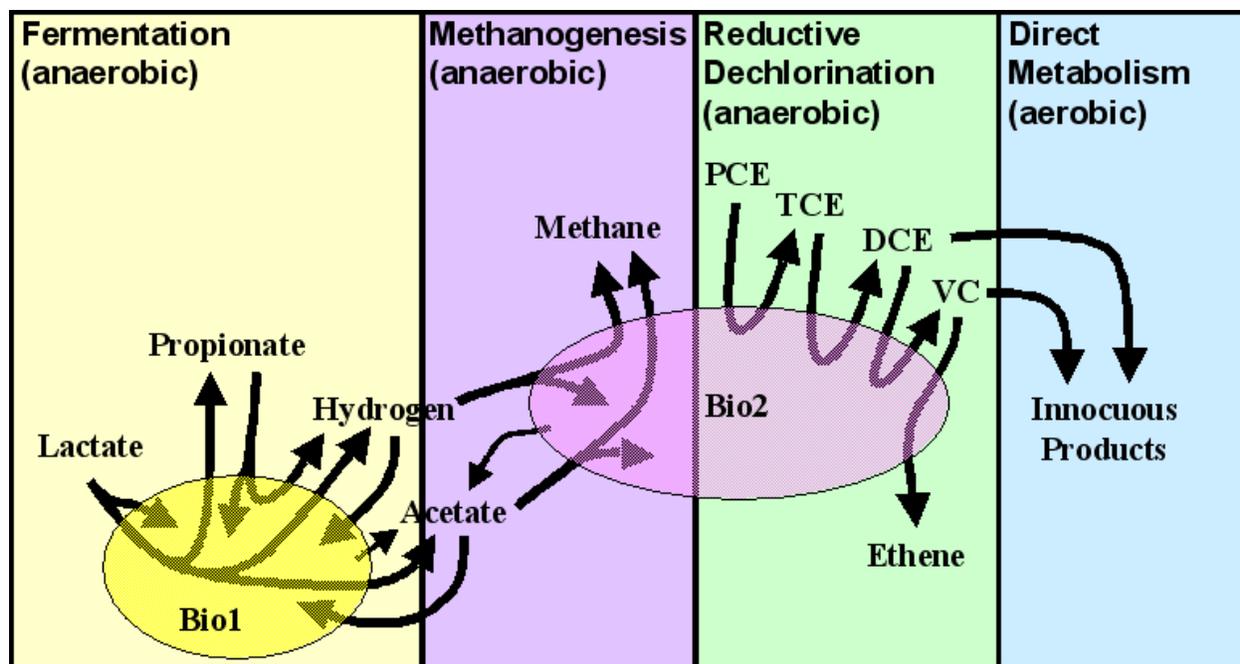


Figure 36. *Conceptual Model for the Reductive Dechlorination Reactions of the Substrate-Linked Reductive Dechlorination of Chloroethenes Reaction Module*

8.2 Reaction Equations

The basic functioning of this reaction module is described in this section for the 15 chemical species in Table 41. See Table 42 for a detailed itemization of all reaction parameters used in this reaction module.

If oxygen is present, the module first uses instantaneous (equilibrium) stoichiometric reactions (Equations 126 to 128) to deplete oxygen by reaction with the organic acids. The module has provisions to sequentially oxidize organic acids in the order of lactate, propionate, and acetate to the point where either all oxygen is consumed or all organic acids are consumed. The initial concentrations for lactate, propionate, acetate, and oxygen $[\text{Species}]_{\text{ox}}$, which are used in the subsequent biomass growth and dechlorination rate calculations. The sum of the residual lactate, propionate, and acetate is calculated as the organic acid concentration $[\text{OrgAcid}]$, which is used in the determination of the organic acid inhibition term. Oxygen, $[\text{OXY}]_{\text{ox}}$, inhibits anaerobic reactions and also must be present for aerobic degradation of DCE and VC. However, the module does not consider consumption of oxygen during DCE or VC oxidation.



Inhibition of biomass growth because of the presence of oxygen (InhibOxy) and organic acids (InhibOA1 and InhibOA2 for Bio1 and Bio2, respectively) is calculated based on a sigmoidal function. When the relevant concentration ($[\text{OXY}]_{\text{ox}}$ or $[\text{OrgAcid}]$) is at 90% of the inhibition coefficient value (k_{i0} , k_{i1} , or k_{i2}), the inhibition term is equal to a value of 1.0. When the relevant concentration is at 110% of the inhibition coefficient value, then the fractional inhibition term has a value of 0.0. The fractional inhibition terms follow a sigmoidal functionality between those points, as shown in Figure 37. Conversely, the PromoOxy term acts in the opposite manner to allow aerobic reactions at concentrations above the value of k_{i0} . The biomass decay rate is attenuated as the biomass concentration approaches the minimum in a similar manner by setting the f_{dec1} and f_{dec2} fractional terms for Bio1 and Bio2, respectively, to 0.0 at the minimum biomass concentration and to 1.0 at 120% of the minimum biomass concentration.

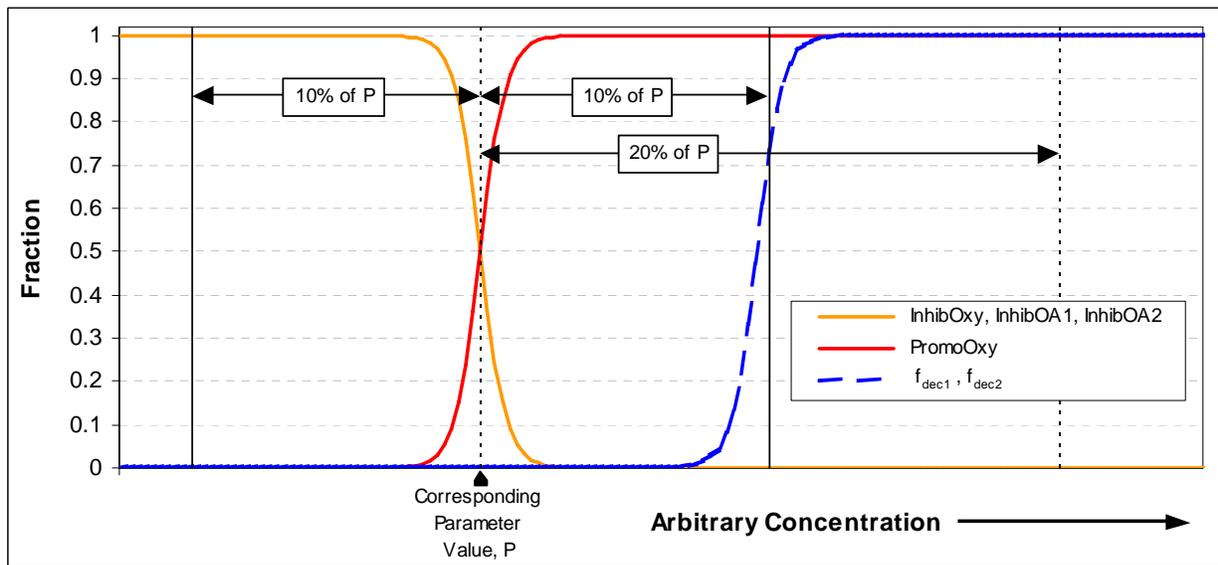


Figure 37. *Conceptual Diagram of the Behavior of the Function Representing a Change in Conditions as a Smooth Transition in the Form of a Sigmoidal Curve — This diagram depicts the trend for the various groups of parameters; the actual curves will be shifted on the X-axis based on the corresponding target concentration.*

Monod growth kinetics with inhibition by oxygen and organic acids are used to compute growth of fermentors (Bio1) and methanogens (Bio2) for the different potential substrates (Equations 129 through 134).

$$r_1 = \mu_{l1} \cdot [Bio1] \cdot \left(\frac{[Lac]_{ox}}{K_{l1} + [Lac]_{ox}} \right) \cdot InhibOxy \cdot InhibOA1 \quad (129)$$

$$r_2 = \mu_{p1} \cdot [Bio1] \cdot \left(\frac{[Pro]_{ox}}{K_{p1} + [Pro]_{ox}} \right) \cdot InhibOxy \cdot InhibOA1 \quad (130)$$

$$r_3 = \mu_{a2} \cdot [Bio2] \cdot \left(\frac{[Ace]_{ox}}{K_{a2} + [Ace]_{ox}} \right) \cdot InhibOxy \cdot InhibOA2 \quad (131)$$

$$r_4 = \mu_{h2} \cdot [Bio2] \cdot \left(\frac{[H2]}{K_{h2} + [H2]} \right) \cdot InhibOxy \cdot InhibOA2 \quad (132)$$

$$r_5 = \mu_{a1} \cdot [Bio1] \cdot \left(\frac{[Ace]_{ox}}{K_{a1} + [Ace]_{ox}} \right) \cdot InhibOxy \cdot InhibOA1 \quad (133)$$

$$r_7 = \mu_{h1} \cdot [Bio1] \cdot \left(\frac{[H2]}{K_{h1} + [H2]} \right) \cdot InhibOxy \cdot InhibOA1 \quad (134)$$

Equations 135 through 149 describe the rate of concentration change for each chemical species. These equations include the consumption/transformation/production based on the biomass growth, oxidation of the organic acids, biomass decay, and aerobic destruction of lesser-chlorinated ethenes. Aerobic degradation of DCE and VC only occurs in the presence of oxygen (if sufficient oxygen remains after oxidation of organic acids) and is modeled as a first-order process (see the conceptual model description of the Mixed Chloroethene/Chloroethane/Chloromethane Dechlorination reaction module for discussion on the assumption of first-order reaction kinetics). A fraction of the decayed biomass is assumed to be converted to acetate, which is then available to support biomass growth. Anaerobic dechlorination of TCE, DCE, and VC are inhibited by the presence of higher-chlorinated ethene species proportional to the ratio of the species to the sum of the species plus all higher-chlorinated species.

$$\frac{d[LAC]}{dt} = -r_1 \cdot \left(\frac{1}{F_{xy/LAC}} \right) \quad (135)$$

$$\frac{d[PRO]}{dt} = r_1 \cdot \left(\frac{F_{PRO/LAC}}{F_{xy/LAC}} \right) - r_2 \cdot \left(\frac{1}{F_{xy/PRO}} \right) \quad (136)$$

$$\begin{aligned} \frac{d[ACE]}{dt} = & r_1 \cdot \left(\frac{F_{ACE/LAC}}{F_{XY/LAC}} \right) + r_2 \cdot \left(\frac{F_{ACE/PRO}}{F_{XY/PRO}} \right) - r_3 \cdot \left(\frac{1}{F_{X2/ACE}} \right) - r_5 \cdot \left(\frac{1}{F_{XY/ACE}} \right) \\ & + F_{ACE/X} \cdot f_{dk2ace} \cdot (f_{dec1} \cdot k_{dec1} \cdot [Bio1] + f_{dec2} \cdot k_{dec2} \cdot [Bio2]) \end{aligned} \quad (137)$$

$$\frac{d[H2]}{dt} = r_1 \cdot \left(\frac{F_{H2/LAC}}{F_{XY/LAC}} \right) + r_2 \cdot \left(\frac{F_{H2/PRO}}{F_{XY/PRO}} \right) - r_4 \cdot \left(\frac{1}{F_{X2/H2}} \right) - r_7 \cdot \left(\frac{1}{F_{XY/H2}} \right) \quad (138)$$

$$\frac{d[MET]}{dt} = qq = r_3 \cdot \left(\frac{F_{MET/ACE}}{F_{X2/ACE}} \right) + r_4 \cdot \left(\frac{F_{MET/H2}}{F_{X2/H2}} \right) \quad (139)$$

$$\frac{d[PCE]}{dt} = -qq \cdot F_{PCE/MET} \cdot \left(\frac{[PCE]}{K_{PCE} + [PCE]} \right) \quad (140)$$

$$\frac{d[TCE]}{dt} = qq \cdot \left[F_{PCE/MET} \cdot \left(\frac{[PCE]}{K_{PCE} + [PCE]} \right) - F_{TCE/MET} \cdot \left(\frac{[TCE]}{K_{TCE} + [TCE]} \right) \cdot \left(\frac{[TCE]}{[PCE] + [TCE]} \right) \right] \quad (141)$$

$$\begin{aligned} \frac{d[DCE]}{dt} = & qq \cdot F_{TCE/MET} \cdot \left(\frac{[TCE]}{K_{TCE} + [TCE]} \right) \cdot \left(\frac{[TCE]}{[PCE] + [TCE]} \right) \\ & - qq \cdot F_{DCE/MET} \cdot \left(\frac{[DCE]}{K_{DCE} + [DCE]} \right) \cdot \left(\frac{[DCE]}{[PCE] + [TCE] + [DCE]} \right) \\ & - ka e_{DCE} \cdot [DCE] \cdot PromoOxy \end{aligned} \quad (142)$$

$$\begin{aligned} \frac{d[VC]}{dt} = & qq \cdot F_{DCE/MET} \cdot \left(\frac{[DCE]}{K_{DCE} + [DCE]} \right) \cdot \left(\frac{[DCE]}{[PCE] + [TCE] + [DCE]} \right) \\ & - qq \cdot F_{VC/MET} \cdot \left(\frac{[VC]}{K_{VC} + [VC]} \right) \cdot \left(\frac{[VC]}{[PCE] + [TCE] + [DCE] + [VC]} \right) \\ & - ka e_{VC} \cdot [VC] \cdot PromoOxy \end{aligned} \quad (143)$$

$$\frac{d[ETH]}{dt} = qq \cdot F_{VC/MET} \cdot \left(\frac{[VC]}{K_{VC} + [VC]} \right) \cdot \left(\frac{[VC]}{[PCE] + [TCE] + [DCE] + [VC]} \right) \quad (144)$$

$$\frac{d[OXY]}{dt} = 0.0 \quad \text{(Oxygen is consumed by equilibrium oxidation reactions, but kinetic consumption of oxygen during DCE or VC biodegradation is not tracked because those are modeled as first-order processes.)} \quad (145)$$

$$\frac{d[Tracer]}{dt} = 0.0 \quad \text{(Conservative [non-reactive] tracer.)} \quad (146)$$

$$\frac{d[Bio1]}{dt} = r_2 + r_5 + r_1 + r_7 - f_{dec1} \cdot k_{dec1} \cdot [Bio1] \quad (147)$$

$$\frac{d[Bio2]}{dt} = r_3 + r_4 - f_{dec2} \cdot k_{dec2} \cdot [Bio2] \quad (148)$$

$$\frac{d[BioT]}{dt} = r_2 + r_5 + r_1 + r_7 + r_3 + r_4 - f_{dec1} \cdot k_{dec1} \cdot [Bio1] - f_{dec2} \cdot k_{dec2} \cdot [Bio2] \quad (149)$$

8.3 Required Input

The reaction parameters for this reaction module are made available to RT3D as part of the input for the Reaction Package. The Reaction Package input file structure is discussed in the RT3D manual and addendum [Clement, 1997; Clement and Johnson, 2002]. The 44 reaction parameters that must be specified for this reaction module are listed in Table 42 in the required order (ID Number) with units and a description. Site-specific knowledge from field data or laboratory tests should be applied to determine an appropriate model configuration for reaction parameters (i.e., the values and the spatial distribution).

Table 42. Input Parameters for the Substrate-Linked Reductive Dechlorination of Chloroethenes Reaction Module

ID #	Parameter	Fortran Variable	Units	Description
1	$Bio1_{min}$	minbio1	mg-DW/L	Minimum (background) biomass concentration for “fermentors”
2	$Bio2_{min}$	minbio2	mg-DW/L	Minimum (background) biomass concentration for methanogens
3	k_{dec1}	kdec1	1/day	First-order decay rate for biomass 1
4	k_{dec2}	kdec2	1/day	First-order decay rate for biomass2
5	μ_{l1}	ul1	1/day	Maximum growth rate for biomass 1 on lactate
6	μ_{p1}	up1	1/day	Maximum growth rate for biomass 1 on propionate
7	μ_{a2}	ua2	1/day	Maximum growth rate for biomass 2 on acetate
8	μ_{h2}	uh2	1/day	Maximum growth rate for biomass 2 on hydrogen
9	μ_{a1}	ua1	1/day	Maximum growth rate for biomass 1 on acetate

Table 42. (contd)

ID #	Parameter	Fortran Variable	Units	Description
10	μ_{h1}	uh1	1/day	Maximum growth rate for biomass 1 on hydrogen
11	k_{i1}	ki1	mg/L	Inhibition coefficient for organic acids on biomass 1
12	k_{i2}	ki2	mg/L	Inhibition coefficient for organic acids on biomass 2
13	k_{io}	kio	mg/L	Inhibition coefficient for oxygen on anaerobic activity
14	K_{l1}	Kl1	mg/L	Monod half-saturation coefficient for “fermentor” growth on lactate
15	K_{p1}	Kp1	mg/L	Monod half-saturation coefficient for “fermentor” growth on propionate
16	K_{a2}	Ka2	mg/L	Monod half-saturation coefficient for methanogen growth on acetate
17	K_{h2}	Kh2	mg/L	Monod half-saturation coefficient for methanogen growth on hydrogen
18	K_{a1}	Ka1	mg/L	Monod half-saturation coefficient for “fermentor” growth on acetate
19	K_{h1}	Kh1	mg/L	Monod half-saturation coefficient for “fermentor” growth on hydrogen
20	K_{PCE}	Kpce	mg/L	Monod half-saturation coefficient for PCE dechlorination
21	K_{TCE}	Ktce	mg/L	Monod half-saturation coefficient for TCE dechlorination
22	K_{DCE}	Kdce	mg/L	Monod half-saturation coefficient for DCE dechlorination
23	K_{VC}	Kvc	mg/L	Monod half-saturation coefficient for VC dechlorination
24	f_{dk2ace}	fdk2ace	--	Fraction of biomass that can decay to produce acetate
25	$F_{ACE/x}$	f_ace_x	mol/mol	Moles of acetate formed per mole of biomass decayed
26	$F_{x/LAC}$	f_x1_lac	mol/mol	Moles of biomass1 formed per mole of lactate
27	$F_{x/PRO}$	f_x1_pro	mol/mol	Moles of biomass1 formed per mole of propionate
28	$F_{x/ACE}$	f_x1_ace	mol/mol	Moles of biomass1 formed per mole of acetate
29	F_{x/H_2}	f_x1_h2	mol/mol	Moles of biomass1 formed per mole of hydrogen
30	$F_{x2/ACE}$	f_x2_ace	mol/mol	Moles of biomass2 formed per mole of acetate
31	F_{x2/H_2}	f_x2_h2	mol/mol	Moles of biomass2 formed per mole of hydrogen
32	$F_{x/LAC}$	f_ace_lac	mol/mol	Moles of acetate formed per mole of lactate
33	$F_{x/LAC}$	f_pro_lac	mol/mol	Moles of propionate formed per mole of lactate

Table 42. (contd)

ID #	Parameter	Fortran Variable	Units	Description
34	$F_{xy/LAC}$	f_h2_lac	mol/mol	Moles of hydrogen formed per mole of lactate
35	$F_{xy/LAC}$	f_ace_pro	mol/mol	Moles of acetate formed per mole of propionate
36	$F_{xy/LAC}$	f_h2_pro	mol/mol	Moles of hydrogen formed per mole of propionate
37	$F_{xy/LAC}$	f_met_ace	mol/mol	Moles of methane formed per mole of acetate
38	$F_{xy/LAC}$	f_met_h2	mol/mol	Moles of methane formed per mole of hydrogen
39	$F_{PCE/MET}$	f_pce_met	mol/mol	Moles of PCE dechlorinated per mole methanogenic biomass increase
40	$F_{TCE/MET}$	f_tce_met	mol/mol	Moles of TCE dechlorinated per mole methanogenic biomass increase
41	$F_{DCE/MET}$	f_dce_met	mol/mol	Moles of DCE dechlorinated per mole methanogenic biomass increase
42	$F_{VC/MET}$	f_vc_met	mol/mol	Moles of VC dechlorinated per mole methanogenic biomass increase
43	kae_{DCE}	kae_dce	1/day	First-order decay coefficient for aerobic dechlorination of DCE
44	kae_{VC}	kae_vc	1/day	First-order decay coefficient for aerobic dechlorination of VC

8.4 Example Simulations

Simulations with this reaction module were conducted with RT3D in a batch reactor (no flow) mode to show examples of how the reaction module simulates the pattern of dechlorination. The parameter values for each example simulation are listed in Tables 43 through 45. These parameters are arbitrary values and are not directly related to any specific laboratory data. Site-specific values would need to be determined as part of a calibration process. Results for these example batch simulations are shown in the Figures 38 through 42, respectively.

Table 43. Parameter Values for Example Simulation 1 with the Substrate-Linked Reductive Dechlorination of Chloroethenes Reaction Module

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	minbio1	0.5	mgDW/L	23	Kvc	10	mg/L
2	minbio2	0.05	mgDW/L	24	fdk2ace	0.2	–
3	kdec1	0.023	1/day	25	f_ace_x	0.25	mol/mol
4	kdec2	0.002	1/day	26	f_x1_lac	0.05	mol/mol
5	ul1	0.1	1/day	27	f_x1_pro	0.1	mol/mol
6	up1	0.01	1/day	28	f_x1_ace	0.1	mol/mol
7	ua2	0.001	1/day	29	f_x1_h2	0.01	mol/mol
8	uh2	0.1	1/day	30	f_x2_ace	0.1	mol/mol
9	ua1	0.001	1/day	31	f_x2_h2	0.1	mol/mol
10	uh1	0.001	1/day	32	f_ace_lac	0.7	mol/mol
11	ki1	500	mg/L	33	f_pro_lac	0.4	mol/mol
12	ki2	500	mg/L	34	f_h2_lac	0.1	mol/mol
13	kio	0.1	mg/L	35	f_ace_pro	1	mol/mol
14	Kl1	15	mg/L	36	f_h2_pro	3	mol/mol
15	Kp1	15	mg/L	37	f_met_ace	1	mol/mol
16	Ka2	15	mg/L	38	f_met_h2	0.25	mol/mol
17	Kh2	0.01	mg/L	39	f_pce_met	0.4	mol/mol
18	Ka1	15	mg/L	40	f_tce_met	0.3	mol/mol
19	Kh1	0.1	mg/L	41	f_dce_met	0.2	mol/mol
20	Kpce	10	mg/L	42	f_vc_met	0.05	mol/mol
21	Ktce	10	mg/L	43	kae_dce	0.05	1/day
22	Kdce	10	mg/L	44	kae_vc	0.05	1/day

Table 44. Parameter Values for Example Simulation 2 with the Substrate-Linked Reductive Dechlorination of Chloroethenes Reaction Module

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	minbio1	0.5	mgDW/L	23	Kvc	10	mg/L
2	minbio2	0.05	mgDW/L	24	fdk2ace	0.2	–
3	kdec1	0.023	1/day	25	f_ace_x	0.25	mol/mol
4	kdec2	0.002	1/day	26	f_x1_lac	0.05	mol/mol
5	ul1	0.1	1/day	27	f_x1_pro	0.1	mol/mol
6	up1	0.01	1/day	28	f_x1_ace	0.1	mol/mol
7	ua2	0.001	1/day	29	f_x1_h2	0.01	mol/mol
8	uh2	0.1	1/day	30	f_x2_ace	0.1	mol/mol
9	ua1	0.001	1/day	31	f_x2_h2	0.1	mol/mol
10	uh1	0.001	1/day	32	f_ace_lac	0.7	mol/mol
11	ki1	500	mg/L	33	f_pro_lac	0.4	mol/mol
12	ki2	500	mg/L	34	f_h2_lac	0.1	mol/mol
13	kio	0.1	mg/L	35	f_ace_pro	1	mol/mol
14	Kl1	15	mg/L	36	f_h2_pro	3	mol/mol
15	Kp1	15	mg/L	37	f_met_ace	1	mol/mol
16	Ka2	15	mg/L	38	f_met_h2	0.25	mol/mol
17	Kh2	0.01	mg/L	39	f_pce_met	0.4	mol/mol
18	Ka1	15	mg/L	40	f_tce_met	0.3	mol/mol
19	Kh1	0.1	mg/L	41	f_dce_met	0.3	mol/mol
20	Kpce	10	mg/L	42	f_vc_met	0.3	mol/mol
21	Ktce	10	mg/L	43	kae_dce	0.05	1/day
22	Kdce	10	mg/L	44	kae_vc	0.05	1/day

Table 45. *Parameter Values for Example Simulation 3 with the Substrate-Linked Reductive Dechlorination of Chloroethenes Reaction Module*

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	minbio1	0.5	mgDW/L	23	Kvc	10	mg/L
2	minbio2	0.05	mgDW/L	24	fdk2ace	0.2	–
3	kdec1	0.023	1/day	25	f_ace_x	0.25	mol/mol
4	kdec2	0.002	1/day	26	f_x1_lac	0.05	mol/mol
5	ul1	0.05	1/day	27	f_x1_pro	0.1	mol/mol
6	up1	0.005	1/day	28	f_x1_ace	0.1	mol/mol
7	ua2	0.001	1/day	29	f_x1_h2	0.01	mol/mol
8	uh2	0.1	1/day	30	f_x2_ace	0.1	mol/mol
9	ua1	0.0005	1/day	31	f_x2_h2	0.1	mol/mol
10	uh1	0.0005	1/day	32	f_ace_lac	0.7	mol/mol
11	ki1	500	mg/L	33	f_pro_lac	0.4	mol/mol
12	ki2	500	mg/L	34	f_h2_lac	0.1	mol/mol
13	kio	0.1	mg/L	35	f_ace_pro	1	mol/mol
14	Kl1	15	mg/L	36	f_h2_pro	3	mol/mol
15	Kp1	15	mg/L	37	f_met_ace	1	mol/mol
16	Ka2	15	mg/L	38	f_met_h2	0.25	mol/mol
17	Kh2	0.01	mg/L	39	f_pce_met	0.4	mol/mol
18	Ka1	15	mg/L	40	f_tce_met	0.3	mol/mol
19	Kh1	0.1	mg/L	41	f_dce_met	0.2	mol/mol
20	Kpce	10	mg/L	42	f_vc_met	0.05	mol/mol
21	Ktce	10	mg/L	43	kae_dce	0.05	1/day
22	Kdce	10	mg/L	44	kae_vc	0.05	1/day

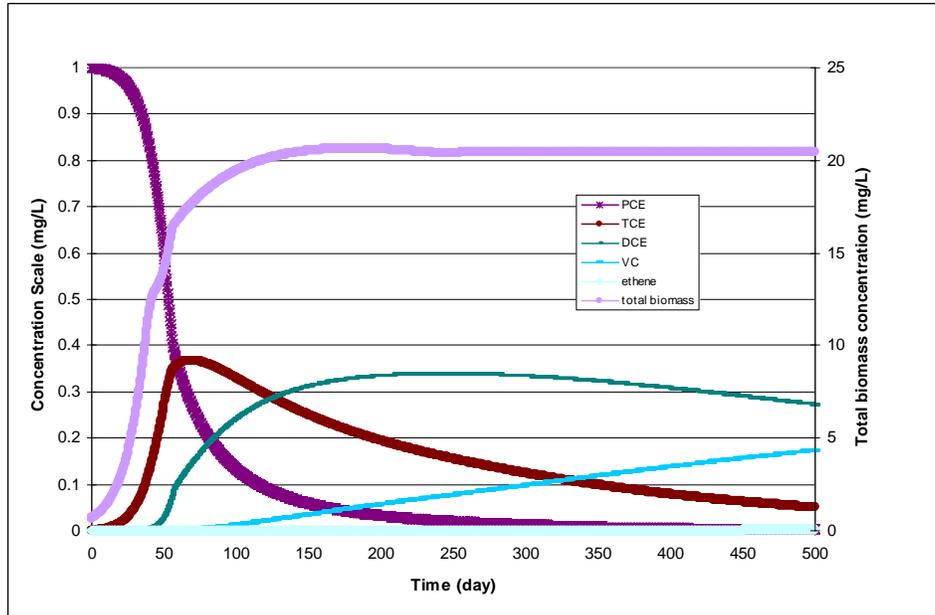


Figure 38. Dechlorination of PCE Using the Parameter Values Shown in Table 43 — The initial concentrations for PCE, lactate, oxygen, Bio1, Bio2, and BioT were 1, 200, 8, 0.6, 0.06, 0.66 mg/L, respectively. All other species concentrations started at zero.

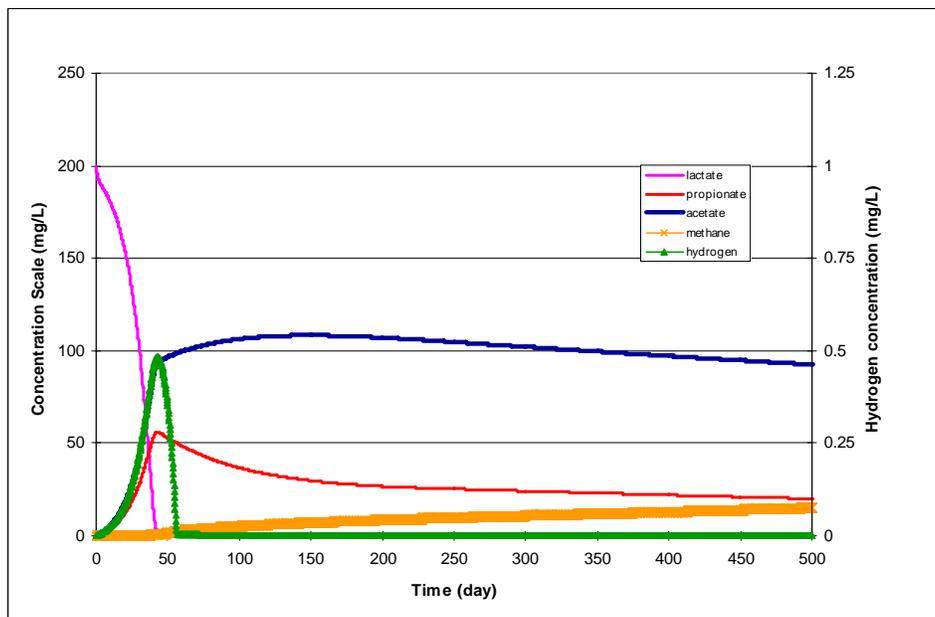


Figure 39. Concentrations of Organic Acids, Hydrogen, and Methane During Dechlorination of PCE Using the Parameter Values Shown in Table 43 — The initial concentrations for PCE, lactate, oxygen, Bio1, Bio2, and BioT were 1, 200, 8, 0.6, 0.06, 0.66 mg/L, respectively. All other species concentrations started at zero.

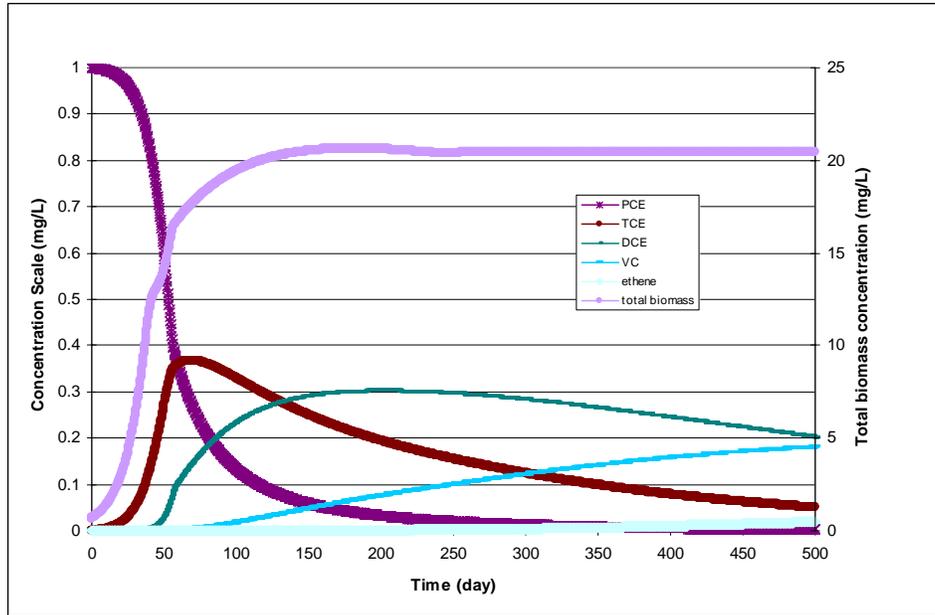


Figure 40. Dechlorination of PCE Using the Parameter Values Shown in Table 44 — The initial concentrations for PCE, lactate, oxygen, Bio1, Bio2, and BioT were 1, 200, 8, 0.6, 0.06, 0.66 mg/L, respectively. All other species concentrations started at zero. The organic acids, hydrogen, and methane results are the same as shown in Figure 39.

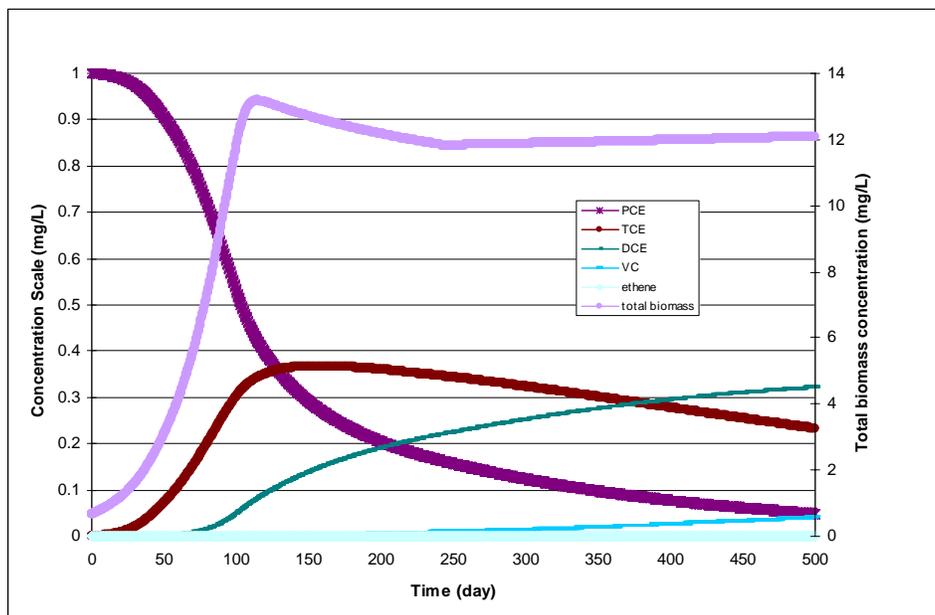


Figure 41. Dechlorination of PCE Using the Parameter Values Shown in Table 45 — The initial concentrations for PCE, lactate, oxygen, Bio1, Bio2, and BioT were 1, 200, 8, 0.6, 0.06, 0.66 mg/L, respectively. All other species concentrations started at zero.

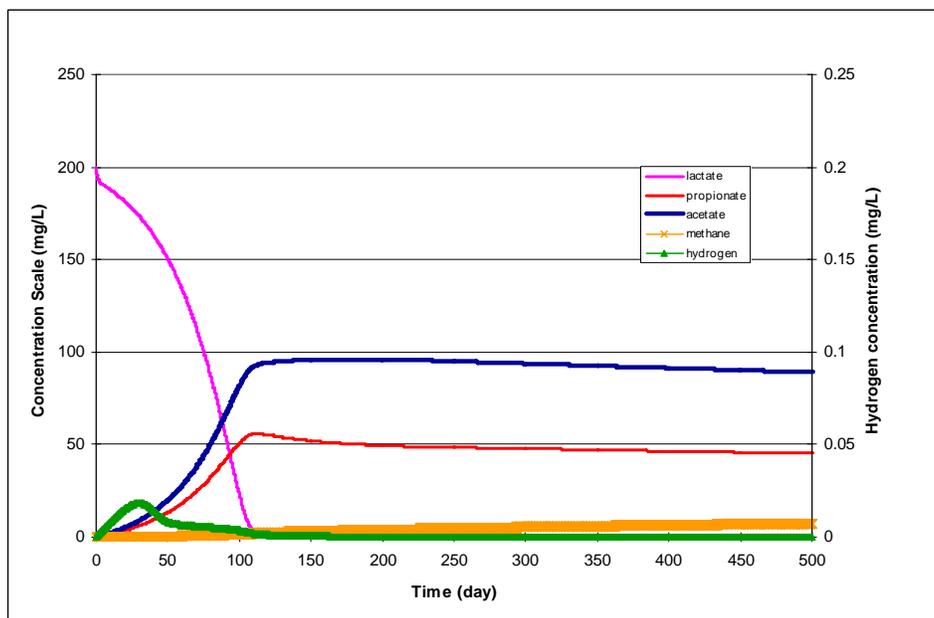


Figure 42. Concentrations of Organic Acids, Hydrogen, and Methane During Dechlorination of PCE Using the Parameter Values Shown in Table 45 — The initial concentrations for PCE, lactate, oxygen, Bio1, Bio2, and BioT were 1, 200, 8, 0.6, 0.06, 0.66 mg/L, respectively. All other species concentrations started at zero.

9.0 Cometabolic Aerobic Dechlorination of Chloroethenes

9.1 Conceptual Model for Dechlorination Reactions

This reaction module describes aerobic cometabolic degradation of trichloroethene, dichloroethene isomers, and chloroethene (vinyl chloride) by methanotrophs. The module includes an explicit description of biomass growth in response to methane and oxygen and tracks both active biomass (which is able to degrade methane and chlorinated ethenes) and total biomass (a combination of active biomass and inactive biomass, the latter of which is not able to degrade methane or chlorinated ethenes). Both types of biomass decay over time according to a user-specified decay rate. This reaction module does not account for changes in porosity/permeability resulting from biomass growth, although the total biomass is also tracked so that the modeler can assess the potential for biological fouling of the aquifer. If required, macroscopic models for biomass-affected porous media properties [Clement et al., 1996] could be combined with this module as a user-defined reaction module to account for changes in porosity/permeability. The cometabolic chlorinated ethene degradation reaction is dependent on the concentration of the chlorinated ethene compound and biomass, is inhibited by methane, requires oxygen, and deactivates biomass (i.e., the module indirectly accounts for destruction of the monooxygenase enzyme by the chlorinated ethene degradation intermediate epoxide compounds). The reaction rate expressions are based on the approach of Semprini et al. [1991], who reported kinetic expressions that include methane inhibition of chlorinated ethene degradation. The rate of chlorinated ethene degradation is described with a "transformation capacity" term [Alvarez-Cohen and McCarty, 1991; Chang and Alvarez-Cohen, 1996] incorporated to represent the inactivation of enzyme as a function of the amount of chlorinated ethene degraded. The module also allows the user to input the maximum concentration of methane and oxygen in water, making it possible to model supersaturated conditions, if desired.

Table 46 lists the chemical species included in this reaction module. Figure 43 shows the conceptual model describing the degradation reactions modeled in this reaction module.

Table 46. Chemical Species Included in the Cometabolic Aerobic Dechlorination of Chloroethenes Reaction Module

No.	Abbreviation ^a	Chemical Name	Selected Alternate Name	CAS ^b Registry Number	Molecular Weight ^c (g/mol)	Chemical Formula
1	MET	Methane	—	74-82-8	16.04246	CH ₄
2	OXY	Oxygen (dimer)	—	7782-44-7	31.9988	O ₂
3	TCE	Trichloroethene	Trichloroethylene	79-01-6	131.38834	C ₂ HCl ₃
4	DCE	Dichloroethene (all isomers)	Dichloroethylene	156-59-2	96.94328	C ₂ H ₂ Cl ₂
5	VC	Chloroethene	Vinyl Chloride	75-01-4	62.49822	C ₂ H ₃ Cl
6	Tracer	Conservative Tracer	—	N/A	N/A	N/A
7	BioA	Active Biomass	Active methanotrophs	—	113.11458	C ₅ H ₇ O ₂ N
8	BioT	Total Biomass	Active and inactive methanotrophs	—	113.11458	C ₅ H ₇ O ₂ N

^a These abbreviations refer to the specific chemicals listed here and should not be confused with different chemicals that may use the same abbreviation in other reaction modules.

^b CAS = Chemical Abstracts Service (see <http://www.cas.org/EO/regsys.html>)

^c Based on International Union of Pure and Applied Chemistry values reported by Loss [2003].

N/A – Not Applicable

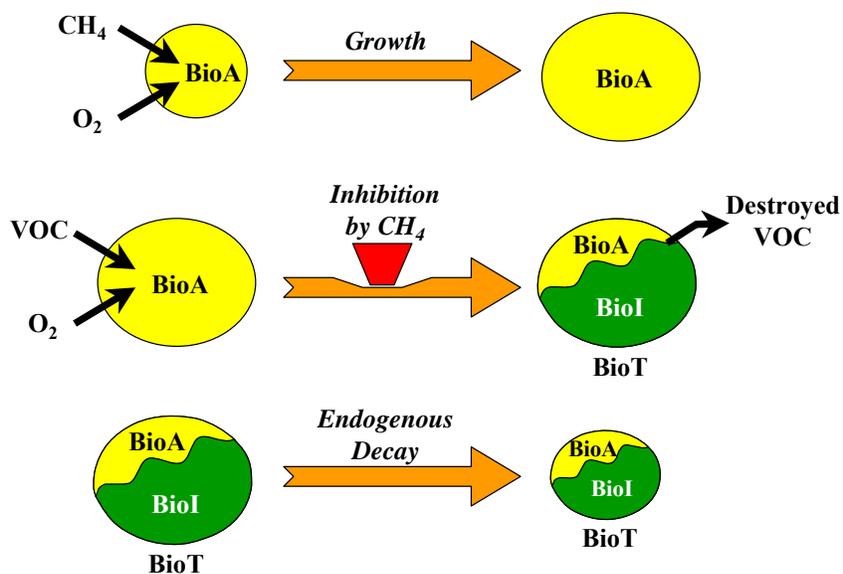


Figure 43. Conceptual Model for Biomass Growth, Decay, and Cometabolic Degradation Reactions — Active biomass (BioA) grows, contributing to the total biomass (BioT). Active biomass can destroy VOCs (i.e., TCE, DCE, and/or VC), resulting in inactivation of a portion of the biomass (BioI). The rate of VOC destruction is inhibited by the presence of methane. Biomass will also die and decay.

The conceptual model for biomass growth and chlorinated ethene destruction requires the presence of dissolved oxygen. Methane is metabolized by the active biomass to produce additional active biomass. TCE, DCE, and VC are destroyed by active biomass, and in the process, some of the biomass is inactivated. The TCE, DCE, VC destruction process is inhibited by methane. Active and inactive biomass both decay at a user-specified first-order decay rate.

9.2 Reaction Equations

The reaction kinetics for the conceptual model described above are presented in Equations 150 through 157. These equations represent the change in concentration over time for the 8 chemical species in Table 46. Table 47 provides a detailed itemization of all user-specified reaction parameters used in this reaction module.

Active biomass is inactivated by the chlorinated ethene destruction reactions at a ratio defined by the user-specified transformation capacity. Monod-like terms are used to implement methane inhibition of chlorinated ethene destruction. A Monod term for methane represents its importance to biomass growth. Similarly, a Monod term for oxygen is used to require the presence of oxygen for both biomass growth and chlorinated ethene destruction. The rate of chlorinated ethene destruction depends on the concentration of the chlorinated ethenes as well. The rates of all consumption/destruction/growth reactions depend on the concentration of active biomass. The active biomass and total biomass are restricted to have a concentration of at least the user-specified minimum biomass. A logistic function is used to define f_{dec1} and f_{dec2} as fractional values ranging from 0.0 to 1.0 so that as biomass decays, the biomass concentration smoothly approaches the specified minimum. Dechlorination is allowed to proceed to the point where the active biomass is reduced to the minimum biomass concentration, but additional restrictions on the inactivation of biomass (involving $maxdx$ in Equation 156) prevent the active biomass concentration from going below the minimum biomass. The maximum concentrations of methane and oxygen are limited to the user-specified water solubilities. It is assumed that additional methane or oxygen would volatilize and leave the system. The user can accommodate super-saturation (i.e., using pure oxygen instead of air) by setting higher water solubility limits.

$$\frac{d[MET]}{dt} = -r_{MET} \quad (150)$$

$$\frac{d[OXY]}{dt} = -r_{MET} \cdot F_{\%M} \quad (151)$$

$$\frac{d[TCE]}{dt} = -r_{TCE} = -\mu_{TCE} \cdot \left[\frac{[TCE]}{K_{TCE} \cdot \left(\frac{K_m + [MET]}{K_m} \right) + [TCE]} \right] \cdot \left(\frac{[OXY]}{K_{O_2} + [OXY]} \right) \cdot maxdx \quad (152)$$

$$\frac{d[DCE]}{dt} = -r_{DCE} = -\mu_{DCE} \cdot \left[\frac{[DCE]}{K_{DCE} \cdot \left(\frac{K_m + [MET]}{K_m} \right) + [DCE]} \right] \cdot \left(\frac{[OXY]}{K_{O_2} + [OXY]} \right) \cdot maxdx \quad (153)$$

$$\frac{d[VC]}{dt} = -r_{VC} = -\mu_{VC} \cdot \left[\frac{[VC]}{K_{VC} \cdot \left(\frac{K_m + [MET]}{K_m} \right) + [VC]} \right] \cdot \left(\frac{[OXY]}{K_{O_2} + [OXY]} \right) \cdot maxdx \quad (154)$$

$$\frac{d[Tracer]}{dt} = 0.0 \quad (Conservative [non-reactive] tracer.) \quad (155)$$

$$\frac{d[BioA]}{dt} = Max(r_{BioA}, -maxdx) \quad (156)$$

$$\frac{d[BioT]}{dt} = F_{x/M} \cdot r_{MET} - f_{dec2} \cdot k_{decay} \cdot [BioT] \quad (157)$$

Where r_{MET} , $maxdx$, and r_{BioA} are defined as in Equations 158 through 160, respectively.

$$r_{MET} = \mu_{max} \cdot [BioA] \cdot \left(\frac{[MET]}{K_m + [MET]} \right) \cdot \left(\frac{[OXY]}{K_{O_2} + [OXY]} \right) \cdot \left(\frac{1}{F_{x/M}} \right) \quad (158)$$

$$maxdx = Max([BioA] - bio_0, 0.0) \quad (159)$$

$$r_{BioA} = F_{x/M} \cdot r_{MET} - f_{dec1} \cdot k_{decay} \cdot [BioA] - \left(\frac{r_{TCE}}{TC_{TCE}} + \frac{r_{DCE}}{TC_{DCE}} + \frac{r_{VC}}{TC_{VC}} \right) \quad (160)$$

9.3 Required Input

The reaction parameters for this reaction module are made available to RT3D as part of the input for the Reaction Package. The Reaction Package input file structure is discussed in the RT3D manual and addendum [Clement, 1997; Clement and Johnson, 2002]. The 18 reaction parameters that must be specified for this reaction module are listed in Table 47 in the required order (ID Number) with units and a description. Site-specific knowledge from field data or laboratory tests should be applied to determine an appropriate model configuration for reaction parameters (i.e., the values and the spatial distribution).

Table 47. Input Parameters for the Cometary Aerobic Dechlorination of Chloroethenes Reaction Module

ID #	Parameter	Fortran Variable	Units	Description
1	bio_0	bio_0	mg/L	Minimum methanotroph biomass concentration
2	k_{decay}	kdecay	1/day	Decay rate for methanotrophs
3	μ_{max}	uMax	1/day	Methanotroph maximum growth rate
4	K_m	Km	mg CH ₄ /L	Monod half-saturation coefficient for methanotroph growth for methane
5	K_{O_2}	Ko2	mg O ₂ /L	Monod half-saturation coefficient for methanotroph growth for oxygen
6	K_{TCE}	Ktce	mg TCE/L	Monod half-saturation coefficient for TCE degradation
7	K_{DCE}	Kdce	mg DCE/L	Monod half-saturation coefficient for DCE degradation
8	K_{VC}	Kvc	mg VC/L	Monod half-saturation coefficient for VC degradation
9	$F_{O/M}$	f_o_m	mol/mol	Moles of oxygen consumed per mole of methane degraded
10	$F_{X/M}$	f_x_m	mol/mol	Moles of biomass formed per mole of methane degraded
11	μ_{TCE}	utce	mg TCE / mg Biomass-day	Maximum specific TCE degradation rate coefficient per unit mass of active bacteria
12	μ_{DCE}	udce	mg DCE / mg Biomass-day	Maximum specific DCE degradation rate coefficient per unit mass of active bacteria
13	μ_{VC}	uvc	mg VC / mg Biomass-day	Maximum specific VC degradation rate coefficient per unit mass of active bacteria
14	TC_{TCE}	tctce	mol TCE / mol Biomass	Transformation capacity for TCE
15	TC_{DCE}	tdce	mol DCE / mol Biomass	Transformation capacity for DCE
16	TC_{VC}	tcvc	mol VC / mol Biomass	Transformation capacity for VC
17	CH_{4max}	maxmet	mg/L	Maximum methane concentration in water
18	O_{2max}	maxoxy	mg/L	Maximum oxygen concentration in water

9.4 Example Simulations

Simulations with this reaction module were conducted with RT3D in a batch reactor (no flow) mode to show examples of how the reaction module simulates the pattern of dechlorination. The parameter values for each example simulation are listed in Table 48. These parameters are arbitrary values and are not directly related to any specific laboratory data. Site-specific values would need to be determined as part of a calibration process. Results for these example batch simulations are shown in the Figures 44 and 45, respectively.

Table 48. Parameter Values for Example Simulations 1 and 2 with the Cometabolic Aerobic Dechlorination of Chloroethenes Reaction Module

ID #	Fortran Variable	Value	Units	ID #	Fortran Variable	Value	Units
1	bio_0	0.01	mg DW/L	10	f_x_m	0.0467	mol/mol
2	kdecay	0.00018	1/day	11	utce	4.2	mg TCE/(mg BioA·day)
3	uMax	0.7	1/day	12	udce	3.1	mg DCE/(mg BioA·day)
4	Km	1.10E-03	mg/L	13	uvc	2	mg VC/(mg BioA·day)
5	Ko2	0.01	mg/L	14	tctce	0.096	mol/mol
6	Ktce	9.0E-03	mg/L	15	tcde	0.26	mol/mol
7	Kdce	6.8E-03	mg/L	16	tcvc	0.41	mol/mol
8	Kvc	4.4E-03	mg/L	17	maxmet	23	mg/L
9	f_o_m	1.767	mol/mol	18	maxoxy	20	mg/L

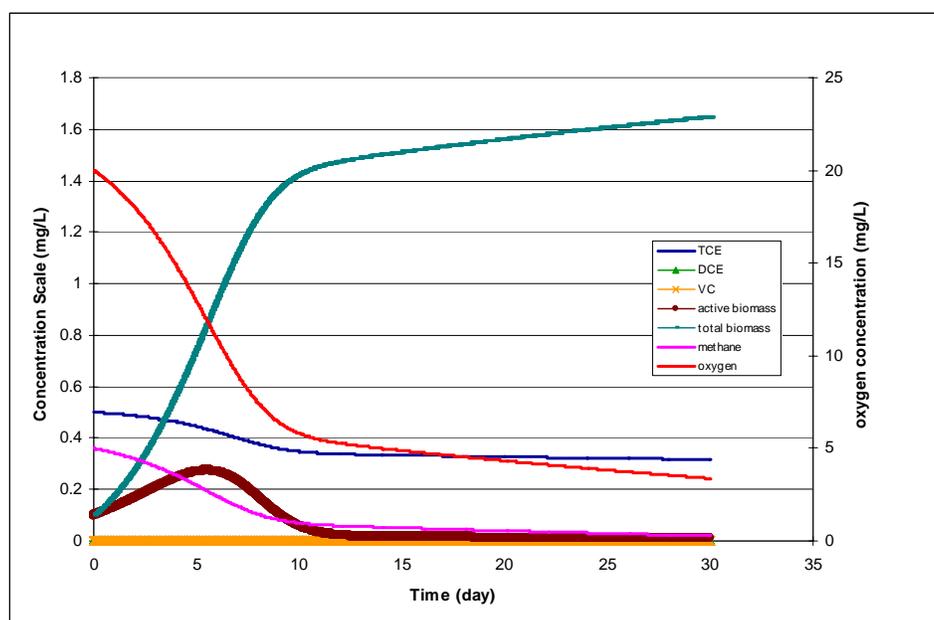


Figure 44. Dechlorination of TCE Using the Parameter Values Shown in Table 48 — The initial concentration for TCE, DCE, VC, methane, oxygen, active biomass, and total biomass were 0.5, 5, 20, 0.1, and 0.1 mg/L, respectively.

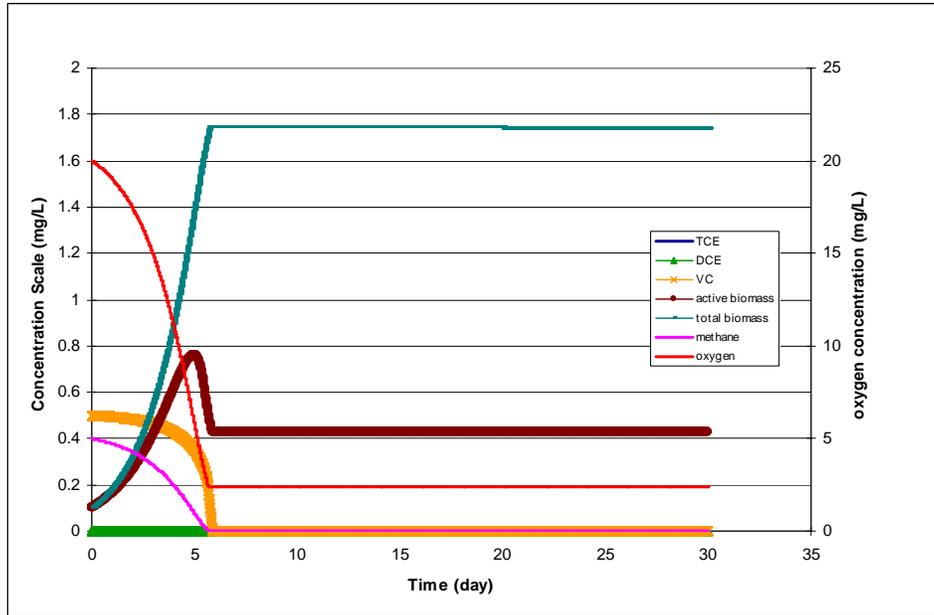


Figure 45. Dechlorination of VC Using the Parameter Values Shown in Table 48 — The initial concentration for VC, methane, oxygen, active biomass, and total biomass were 0.5, 5, 20, 0.1, and 0.1 mg/L, respectively.

10.0 References

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Attachment 3:

rtFlux: RT3D Flux Plane Utility



rtFlux: RT3D Flux Plane Utility

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July 2006

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rtFlux: RT3D Flux Plane Utility

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Summary

A flux plane software utility called rtFlux was developed as a *Microsoft® Excel®*-based pre- and post-processor for a RT3D simulation. The rtFlux utility provides a method for the user to determine the mass flow of chemical species across one or more grid-orthogonal planes over time. Mass flow results are presented as time series plots and as plots showing the spatial distribution of the relative mass flow within a given plane. This document discusses how to install and use the rtFlux software, the calculations that are performed, and gives some examples of the application of the rtFlux utility.

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1.0 Introduction

Monitored natural attenuation (MNA) is an environmental management strategy that relies on a variety of attenuation processes to degrade or immobilize contaminants and is implemented at appropriate sites by demonstrating that contaminant plumes have low risk and are either stable or shrinking. Numerical modelling can be one component of an assessment of MNA or Enhanced Attenuation (EA) (i.e., if MNA is not a viable single remedy). Numerical reactive transport modelling provides a tool with which to quantify the relative stability of a contaminant plume, particularly in cases where simpler evaluations are not suitable because of complex hydrology, past activity at the site, multiple contaminant sources, and/or complex reaction of multiple species. Selection of an appropriate model configuration to represent spatial and temporal variations in site-specific attenuation processes can facilitate assessment of the contaminant loading and attenuation capacity (i.e., mass balance) at the site.

RT3D is a numerical code for simulating three-dimensional multi-species reactive transport in groundwater [Clement, 1997; Clement et al., 1998; Clement and Johnson, 2002; Johnson et al., 2006a]. RT3D can provide information to help analyze the relative importance of different fate and transport processes at an individual site and assess the plume in terms of a mass balance approach. The model can also be used to estimate the future fate and transport of contaminants. These predictions can be valuable input, along with other site information, in making timely decisions regarding implementation of remedial actions or for planning monitoring activities. A key function of the predictive capability of models is to estimate whether the remedy will meet the remediation goals when this determination cannot be made directly with field data.

The typical output from numerical modelling is the spatial distribution of contaminant concentration as time progresses. Such concentration information is the primary metric in determining the success of a remediation scenario with respect to the goal of protecting receptors. However, the mass flux (flow) across a specified plane can provide additional information for making remediation decisions. Mass flux can be a useful indicator of the potential for MNA. Evaluation of the temporal changes in mass flux can reveal the nature of plume migration (expanding, steady state, shrinking) and the time frame to reach a steady state. The mass flux can also be used in quantifying contaminant plume dynamics and the impact of treatment processes. The mass flux from a contamination source defines the amount of attenuation (natural or otherwise) that will be required for a remedy protective of the receptors.

A flux plane software utility called rtFlux was developed as a *Microsoft® Excel®*-based pre- and post-processor for a RT3D simulation. The rtFlux utility provides a method for the user to determine the mass flow of chemical species across one or more grid-orthogonal planes over time. Mass flow results are presented as time series plots and as plots showing the spatial distribution of the relative mass flow terms for a given plane.

Flux planes of interest are defined as rectangular regions that are orthogonal to the model grid (i.e., the plane is aligned parallel to a row, column, or layer of the model grid). The pre-processing step incorporates the flux plane definitions into the RT3D input files. After running RT3D, the output files are processed by the utility to generate three graphs that describe the mass flux across the plane. The first plot shows the time-varying mass flow rate (e.g., kg/day) of each chemical species passing through one of the defined planes. The second plot depicts the cumulative mass that has passed through a plane over time. The underlying data for this plot can be interrogated to obtain a table listing the mass passing through the plane during a specified time interval. The third plot generated from the rtFlux utility is a bubble plot depicting the relative volumetric flow rate, species concentration, or mass flow rate through a plane at each grid cell in a plane. This bubble plot shows the location where the highest mass flux impacts occur, whether due to high volumetric flow rate or a high concentration (or combination of both).

This document discusses how to install and use the rtFlux software, the calculations that are performed, and gives some examples of the application of the rtFlux utility.

2.0 Installation of rtFlux

The rtFlux utility is implemented in two key pieces – a processing engine and a user interface. The processing engine is an executable file that does the behind-the-scenes work of modifying the RT3D input files and processing results. The user interface portion of the rtFlux utility is provided as a *Microsoft® Excel®* template workbook (*.xlt) and is where the user interaction takes place.

2.1 System Requirements

The following hardware and software are required to use the rtFlux utility:

- *IBM®*-compatible personal computer with an *Intel® Pentium®*-compatible processor or greater,
- Monitor resolution of at least 1152 × 864 pixels
- *Microsoft® Windows®* 2000 or *Microsoft® Windows®* XP operating system,
- *Microsoft® Excel®* 2000 or *Microsoft® Excel®* 2003,
- RT3D version 2.5 or greater
- MODFLOW (any version compatible with RT3D)

2.2 Installation

To make the rtFlux interface available in *Microsoft® Excel®*, the template file must be placed (or saved) into the "Templates" directory. The "Templates" directory is typically found in the directory tree at "C:\Documents and Settings\\Application Data\Microsoft\Templates" for recent versions of *Microsoft® Windows®*, where <username> is the actual user name of the current *Windows®* user. A hard drive search may be helpful in determining the actual location of the "Templates" directory.

The processing engine (rtFlux.exe) must be placed in a directory that is in the *Windows®* system search path (defined by the %PATH% environment variable – see your *Windows®* documentation for information on editing environment variables).

2.3 Uninstalling the rtFlux Utility

To uninstall the rtFlux utility, remove (move or delete) the rtFlux template file from the "Templates" directory. This will remove it from the list of document templates in the File/New... dialog box. Removal of the rtFlux.exe file from the directory where you originally placed it will complete the uninstallation.

2.4 Updating to a New Version

Each version of the rtFlux template file will have a unique filename to identify the version of the template (e.g., "rtFlux_1_0_0.xlt"). To update to a newer version, the new template file is placed into the "Templates" directory. If desired, the old template file may be removed from the "Templates" directory. New versions of the processing engine will have the same name as the old version and should directly replace the old version.

3.0 Using the rtFlux Utility

The rtFlux software utility is both a pre-processor and post-processor for a RT3D simulation. The user is assumed to be familiar with both MODFLOW [McDonald and Harbaugh, 1988; Harbaugh et al., 2000; Zheng et al. 2001; Harbaugh, 2005] and RT3D [Clement, 1997; Clement et al., 1998; Clement and Johnson, 2002; Johnson et al., 2006a] as well as the process of defining a model, running the numerical codes, and accessing the resultant output. While MODFLOW and RT3D models are often configured and run from within a third party graphical user interface such as GMS [BYU, 2006], Visual Modflow [WHI, 2005], PMWIN [Chiang, 2005], or Groundwater Vistas [Rumbaugh and Rumbaugh, 2004], the rtFlux software runs external to these groundwater modelling software packages.

The following list summarizes the steps for using the rtFlux utility with an RT3D simulation. Subsequent subsections describe specific actions and the rtFlux toolbar in more detail.

- Configure the MODFLOW model for the site and run MODFLOW. The MODFLOW model must use the LKMT Package [Zheng et al., 2001].
- Configure the RT3D model for the site and save/export the configuration to the RT3D input files.
- In *Excel*[®], create a new rtFlux workbook by selecting the File/New... menu item and opening the rtFlux template file as a new workbook.
- Add data to the "rtFlux_Input" worksheet to define the basic model configuration and the locations for flux planes.
- Export the plane definitions. This will modify the RT3D *.btn input file; any existing observation points in the *.btn file will be deleted. Note that if the RT3D input files are saved/exported from a groundwater modelling software package, the exported plane definitions will be lost.
- Run RT3D. This may be done from within *Excel*[®], from within a groundwater modelling software package (as long as files aren't saved/exported as part of the run command), or from the command prompt (DOS window).
- In *Excel*[®], initiate the action to process the RT3D simulation results and import the flux plane data into the rtFlux workbook. Depending on the size of the model, it may take a while to process the RT3D simulation results. Once the flux information is imported, the user may assess the results displayed on the "Graphs" worksheet.

3.1 Creating a rtFlux Workbook

To generate a new rtFlux workbook, the rtFlux template file is opened from the File/New... menu item. This will create an empty, unsaved document with all of the necessary functionality and will make an "rtFlux" toolbar available. The new document can be saved and subsequently opened in the same manner as any other *Microsoft*[®] *Excel*[®] workbook.

3.2 Saving and Opening a rtFlux Workbook

When first created, a rtFlux workbook is not automatically saved, so the user will need to save the file. When creating or re-opening a rtFlux workbook, the user may receive a message that the workbook contains macros. There are several macros in the rtFlux workbook that are required for calculations to work properly, thus the user should select the "Enable Macros" option. Newer versions of *Microsoft® Excel®* have additional security options found under the Tools/Macro/Security... menu item. If "High Security" is selected, then all macros are disabled by default (with no user prompting) and the rtFlux workbook will not operate correctly. The user should check the security settings and change to "Medium Security" to allow the user to confirm, on an individual workbook basis, whether macros should be enabled or not.

If the user opens a rtFlux workbook with macros disabled, a non-functional rtFlux toolbar will appear. This non-functional rtFlux toolbar must be removed manually from the *Microsoft® Excel®* workspace before the user can once again use a rtFlux workbook properly. To remove the toolbar, close all open rtFlux workbooks and delete the toolbar from the toolbar list shown in the "Customize" dialog box (opened by right clicking on any toolbar and selecting "Customize" or via the Tools/Customize... menu item).

3.3 Description of the rtFlux Toolbar Items

Whenever a rtFlux workbook is created or opened, the "rtFlux" toolbar will appear in the *Microsoft® Excel®* workspace. When the last rtFlux workbook is closed, the rtFlux toolbar will disappear. Figure 1 shows the rtFlux toolbar and the toolbar button functionality is described in Table 1. To insure integrity of the rtFlux utility, **do not** alter the rtFlux toolbar by adding or removing buttons via the Tools/Customize... menu item. Modification of the rtFlux toolbar may cause the associated functions to fail.



Figure 1. *Toolbar for the rtFlux Utility — From left to right the toolbar buttons are: Modify the BTN File to Incorporate Flux Plane Definition(s), Run RT3D, and Process Flux Output and Read Into Excel.*

Table 1. Functionality of the rtFlux Toolbar Buttons

Button	Description
Export Plane Definitions 	This button activates a procedure that examines the plane definitions for validity, exports the plane definitions to a *.job file, and runs the rtFlux engine to incorporate the plane definitions into the *.btn file for the simulation.
Run RT3D 	This button initiates a RT3D simulation run. MODFLOW should have been previously run. RT3D will run for valid model input files regardless of whether flux plane definitions have been exported or not.
Import Results 	This button will start the rtFlux engine to process the RT3D simulation output and generate the flux data; this step may take a while to complete depending on the size of the model. Once the flux data is generated, it is read into the workbook and the plots are set up.

3.4 Defining and Exporting Flux Plane Definitions

To obtain the mass flow through a plane over time from a RT3D simulation, the user must define the flux planes of interest on the "rtFlux_Input" worksheet (Figure 2). Light blue cells on the "rtFlux_Input" worksheet indicate the information to be supplied by the user. Basic information about the model (number of rows, columns, and layers) and the number of flux planes that will be defined are the first items to fill in. The flux planes must be defined as orthogonal to the grid—that is, each plane must be parallel to a row, column, or layer. Flux planes are defined as a rectangular area by specifying the grid cell indices of opposing corners. In effect, this defines the starting and ending rows, columns, and layers for the plane. The standard convention of cell index numbers is used, where the numbers increase from the upper left cell of the top layer (in plan view) to the right (for columns), to the bottom (for rows), and down (for layers). If the plane definition is ambiguous as to the orientation, the user must specify the type of plane (i.e., XY, XZ, or YZ). Each plane is assigned a group identification number automatically, which should not be modified by the user. The Plane Identifier data entry field allows the user to annotate each plane with a name or brief description, but is not actually used elsewhere. Units used in the simulation need not be specified to export the plane definitions, but they are required for importing results.

NCOL:		BTN File:		Conc'n Mass Units:	
NROW:		RT3D Superfile:		Conc'n Volume Units:	
NLAY:		LMKT Output File:		Cubic Grid Length Units:	
Number of Planes:	1	IOB File:		Simulation Time Units:	
				Conversion Factor:	

	Upper Left Corner Cell			Opposing Corner Cell			Unit Definitions	
Plane Identifier	COL	ROW	LAY	COL	ROW	LAY	Group ID	Plane Type

Figure 2. The *rtFlux* Plane Definitions Are Specified Using This Data Entry Layout on the "rtFlux_Input" Worksheet — The lighter blue shading indicates information that must be filled out by the user. The lower block expands to accommodate the number of planes that the user wants to define.

Once defined, plane definitions can be exported to an existing RT3D simulation using the "Export Plane Definitions" button on the *rtFlux* toolbar. In the export process, the plane definitions are validated, exported to an *.iob file, and then incorporated into the *.btn RT3D input file via the *rtFlux* engine. This process takes place automatically aside from the user specifying the location and names for the *.iob file and the *.btn file (which should both be in the same directory). When plane definitions are exported, any existing observation points in the *.btn file will be deleted. Note that if the RT3D input files are saved/exported from a groundwater modelling software package, the exported plane definitions will be lost.

Because the *.iob file is generated automatically, the user will merely need to know that the file is created and that it needs to be saved to the same directory containing the RT3D simulation input files. However, for completeness, the structure of the ASCII text *.iob file is described in Table 2.

Table 2. File Structure for the *.iob File, Containing Flux Plane Definitions

Record	Conditions for Record	Field(s)	Field Description(s)	Format
H1	—	NPLANE	number of planes defined	I10
H2	Repeat this record NPLANE times.	COLS COLE ROWS ROWE LAYS LAYE GRP PTYPE	Starting column of plane Ending column of plane Starting row of plane Ending row of plane Starting layer of plane Ending layer of plane Group ID number for this plane Plane type (XY, XZ, YZ) ID number	7I10

Once the flux plane definitions are successfully exported, RT3D may be executed by the most convenient method. The RT3D executable file must be in a directory that is in the system search path to run RT3D via the *rtFlux* toolbar button in *Excel*[®]. RT3D may be run from within a groundwater modelling software package as long as the run command does not save/export the RT3D input files. More advanced users may prefer to run RT3D from a command prompt (DOS

window). Note that data for the flux plane utility is recorded for every transport step, meaning that the RT3D output files (*.obs) may be large for long or complex simulations.

3.5 Processing and Viewing Flux Plane Results

After running RT3D to produce simulation results, the results can be processed and flux information imported to the rtFlux workbook. The Import Results button on the rtFlux toolbar activates the rtFlux engine to process the RT3D output and generate flux-related data. This step may take a while, depending on the size of the RT3D model (in terms of grid size, number of chemical species, and total simulated time). The user must specify the LKMT output file from the MODFLOW simulation (e.g., *.hff, *.flo) and confirm the *.btn file to use.

Data for the flux planes are imported to tables on a number of worksheets (see Table 3). The "Graphs" worksheet is of primary interest to the user, as it contains the compiled data in three plots and a summary table. The first plot (Figure 1) shows the time-varying mass flow rate (e.g., kg/day) of chemical species at the defined planes. The user may select the chemical species and/or flux plane to display from a drop-down list at the worksheet cells in light blue. The direction of net mass flow is determined by knowing the type of plane (XY, XZ, or YZ) and whether the values are positive (flow in the +x, -y, or -z direction) or negative (flow in the -x, +y, or +z direction). The plot of cumulative mass passing through a plane over time has options similar to those for the mass flow plot.

Table 3. List of Worksheets in a rtFlux Workbook

Worksheet	Information Contained on Worksheet
rtFlux_Input	Flux Plane Definitions
Graphs	Graphs & Tables of Flux Utility Results
Mass_Flow_Data	Data for the Mass Flow Plot
Cumulative_Mass_Data	Data for the Cumulative Mass Plot
Cell_Data	Data for the Bubble Plot
Cumulative_Mass_Positive_Direct	Data for the Cumulative Mass Table
Cumulative_Mass_Negative_Direct	Data for the Cumulative Mass Table

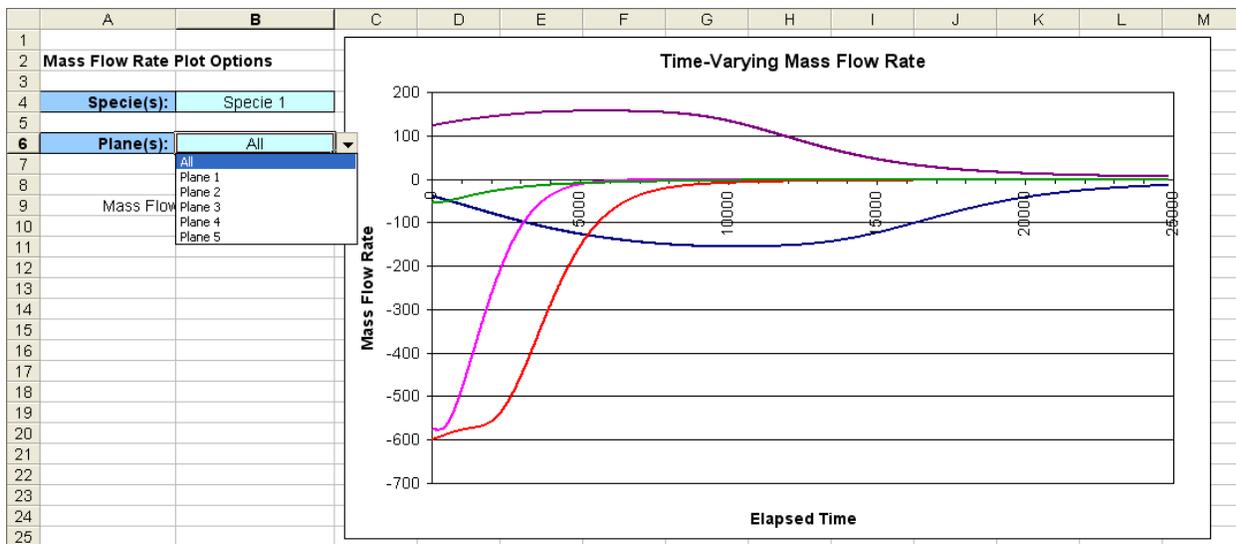


Figure 3. The Time-Varying Mass Flow Rate Plot on the "Graphs" Worksheet — The user may select which species and which plane to view (including all at once) via drop-down selection lists. The cumulative mass flowing through the plane plot is also on the "Graphs" worksheet and is configured similarly.

Figure 4 shows an example of the third plot generated by the rtFlux utility. This bubble plot depicts the relative volumetric flow rate, species concentration, or mass flow rate through a plane at each grid cell in a plane. The user may select the parameter, the species, the plane, and the simulation time to display in the bubble plot. Because *Excel*[®] is limited in the number of rows of data that may be imported, not all transport time points may be imported. The rtFlux utility imports cell-by-cell data for the bubble plot at regularly spaced time points, the frequency of which depends on the total number of grid cells in all the planes and the total number of transport time points. The bubble plot shows the spatial distribution within the plane where the highest mass flux impacts occur. The highest mass flow may be due to a high volumetric flow rate, a high concentration, or a combination of both. The bubbles represent the relative magnitude of the displayed parameter and are scaled relative to the maximum of the entire dataset so changing to a different time point will show the proper relative change in parameter values. The user should be aware that the scaling might cause bubbles for low parameter values to disappear because the relative magnitude is so small. The graph properties can be modified by the user to make small values visible as bubbles at the expense of causing large bubbles to overlap. The bubble plots show the distribution of parameter values in the plane for a uniformly spaced grid. Non-uniform grids or deformed grids will be displayed within a uniform grid.

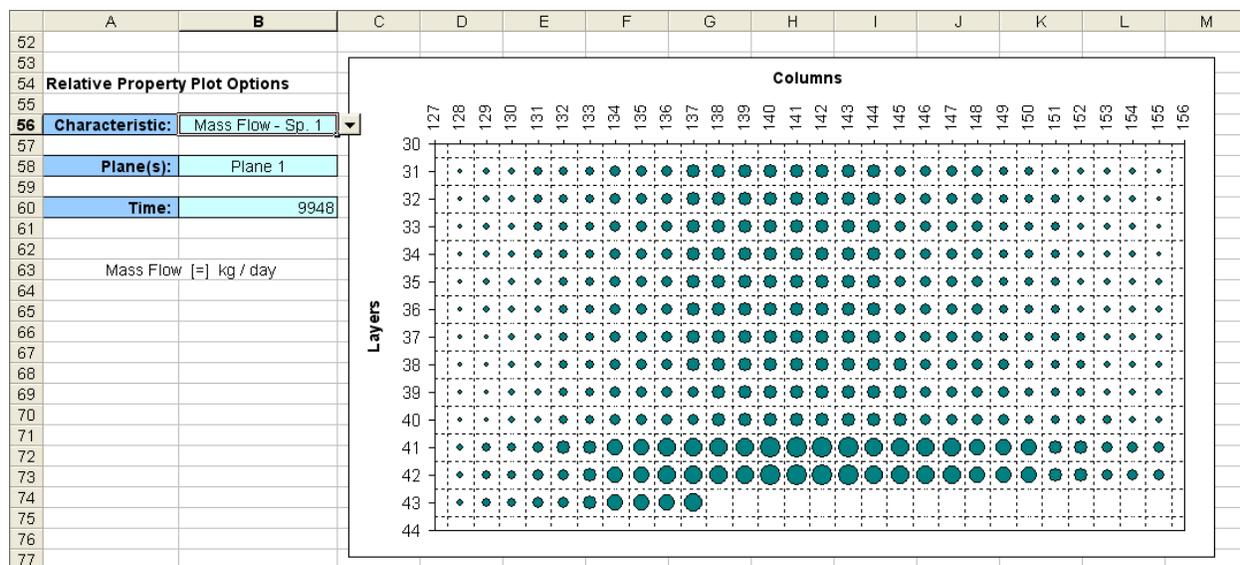


Figure 4. Example of a Bubble Plot Showing the Relative Magnitude of Mass Flow Rate for a Specified Plane at a Particular Time Point in the Simulation — Drop down lists allow the user to select the property (also including volumetric flowrate and concentration), plane, and time to display. The bubble sizes are scaled relative to the largest value in the simulation so that the size shows the proper relative magnitude when looking at different time points.

A summary table of cumulative mass passing through each plane for each species is included at the bottom of the "Graphs" worksheet. This table shows the mass moving in both positive (+x, -y, or -z) and negative (-x, +y, or +z) directions as well as the net cumulative mass passing through each plane (which is what is plotted in the cumulative mass plot). Mass may flow in both directions through a plane depending on the steady state or transient flow characteristics at the location where the plane is defined. Start and end times at points within the time frame of the simulation may be selected via drop-down lists to view the cumulative mass for a specified period. An example of this summary table is shown in Figure 5.

Begin Time:	0
End Time:	24820

Cumulative Mass Flowing Through Plane				
Specie #	Plane #	Total Mass Thru Plane in Positive Direction (kg)	Total Mass Thru Plane in Negative Direction (kg)	Net Mass Thru Plane (kg)
1	1	2091799	-0.353	2091799
1	2	15143.47	-2422723	-2407580
1	3	3.08163	-1210683	-1210680
1	4	743.8011	-2517156	-2516413
1	5	52427.44	-226410	-173983

Figure 5. Example of the Summary Table for Cumulative Mass Flowing Through Each Plane on the "Graphs" Worksheet — This table shows the mass moving in both positive (+x, -y, or -z) and negative (-x, +y, or +z) directions as well as the net cumulative mass passing through each plane. The user may select the start and end times to apply to the table to view the cumulative mass for a specified period.

The remaining worksheets in the rtFlux workbook (Table 3) contain the root data on which the plots and summary table are based. Figures 6 to 8 show partial examples of data on the "Mass_Flow_Data," "Cumulative_Mass_Data," and "Cell_Data" worksheets, respectively. The "Cumulative_Mass_Positive_Direct" and "Cumulative_Mass_Negative_Direct" worksheets are configured the same as the "Cumulative_Mass_Data" worksheet, but contain cumulative mass moving in the positive and negative directions, respectively, instead of the net mass passing through the plane. The user will not typically need to interact with these worksheets. However, the "Cell_Data" worksheet is configured to allow data filtering to make interrogation of the cell-by-cell data set more convenient. Note that filtering of the cell-by-cell data will impact what is displayed in the bubble plot.

Number of Time Steps:	2505
Number of Planes:	5
Number of Species:	1

MASS FLOW RATE

(kg / day)

	Plane # 1	Plane # 2	Plane # 3	Plane # 4	Plane # 5
	Specie #				
	1	1	1	1	1
Elapsed Time	Sp 1, P 1	Sp 1, P 2	Sp 1, P 3	Sp 1, P 4	Sp 1, P 5
0.1	123.308	-38.4394	-575.82	-598.777	-50.8043
10.1	123.4393	-38.6626	-575.909	-598.461	-51.507
20.1	123.5704	-38.8823	-575.987	-598.186	-52.0471
30.1	123.7011	-39.0995	-576.057	-597.931	-52.472
40.1	123.8316	-39.3148	-576.126	-597.695	-52.8111
50.1	123.9617	-39.5284	-576.192	-597.463	-53.0864
60.1	124.0917	-39.7405	-576.258	-597.24	-53.3122
70.1	124.2211	-39.9513	-576.323	-597.018	-53.4991
80.1	124.3503	-40.1609	-576.39	-596.799	-53.6538
90.1	124.4791	-40.3693	-576.457	-596.581	-53.7818
100.1	124.6076	-40.5767	-576.524	-596.363	-53.8861
110.1	124.7361	-40.7832	-576.591	-596.144	-53.9704
120.1	124.8642	-40.9888	-576.657	-595.924	-54.0365

Figure 6. Partial Example of the "Mass_Flow_Data" Worksheet, Where Data for the Mass Flow Rate is Stored

NET CUMULATIVE MASS

(kg)

	Plane # 1	Plane # 2	Plane # 3	Plane # 4	Plane # 5
	Specie #				
	1	1	1	1	1
Elapsed Time	Sp 1, P 1	Sp 1, P 2	Sp 1, P 3	Sp 1, P 4	Sp 1, P 5
0.1	6.165401	-1.92197	-28.791	-29.9388	-2.54022
10.1	1239.902	-387.432	-5787.43	-6016.13	-514.097
20.1	2474.951	-775.157	-11546.9	-11999.4	-1031.87
30.1	3711.308	-1165.07	-17307.1	-17979.9	-1554.46
40.1	4948.971	-1557.14	-23068	-23958.1	-2080.88
50.1	6187.938	-1951.35	-28829.6	-29933.9	-2610.37
60.1	7428.205	-2347.7	-34591.9	-35907.4	-3142.36
70.1	8669.769	-2746.16	-40354.8	-41878.7	-3676.42
80.1	9912.626	-3146.72	-46118.4	-47847.7	-4212.18
90.1	11156.77	-3549.37	-51882.6	-53814.6	-4749.36
100.1	12402.21	-3954.1	-57647.5	-59779.4	-5287.7
110.1	13648.93	-4360.9	-63413.1	-65741.9	-5826.98
120.1	14896.93	-4769.76	-69179.3	-71702.2	-6367.02

Figure 7. Partial Example of the "Cumulative_Mass_Data" Worksheet Holding the Data for Net Cumulative Mass Passing Through the Plane

NOBS: 5082

CELL-BY-CELL DATA

Flow [=] ft³ / day

Conc'n [=] mg / L

Mass Flow [=] kg / day

Elapsed Time	Plane #	Flow Direction	K	I	J	Volumetric Flow	Concentration		Mass Flow	
							Specie # 1	Specie # 1		
0.1	1	2	27	137	123	0.07677077	0.000263013	5.72E-10		
0.1	1	2	27	137	124	0.08001004	0.000266013	6.03E-10		
0.1	1	2	27	137	125	0.08311607	0.000279014	6.57E-10		
0.1	1	2	27	137	126	0.08608488	0.000310019	7.56E-10		
0.1	1	2	27	137	127	0.08891378	0.00290927	7.32E-09		
0.1	1	2	27	137	128	0.09160565	0.00889974	2.31E-08		
0.1	1	2	27	137	129	0.0941678	0.0174664	4.66E-08		
0.1	1	2	27	137	130	0.09660601	0.0316423	8.66E-08		
0.1	1	2	27	137	131	0.09892444	0.0534557	1.5E-07		
0.1	1	2	27	137	132	0.10112538	0.0848855	2.43E-07		
0.1	1	2	27	137	133	0.10320929	0.12765	3.73E-07		
0.1	1	2	27	137	134	0.10517428	0.18258	5.44E-07		
0.1	1	2	27	137	135	0.10701541	0.24997	7.57E-07		
0.1	1	2	27	137	136	0.10872402	0.32865	1.01E-06		
0.1	1	2	27	137	137	0.11028744	0.4167	1.3E-06		
0.1	1	2	27	137	138	0.11168924	0.51103	1.62E-06		
0.1	1	2	27	137	139	0.11290935	0.60804	1.94E-06		

Figure 8. Partial Example of the "Cell_Data" Worksheet — This information is used for the bubble plots of volumetric flowrate, concentration, and mass flow rate on an individual cell basis for a given plane.

4.0 Calculation of Flux Plane Results

The RT3D flux plane utility software performs calculations on concentrations and volumetric flow rates to obtain the net mass flows (e.g., kg/day) through a plane. The term mass flux or flux plane is often mentioned, but differs from a mass flow in that a mass flux is a rate per unit area (e.g., kg/day/m²). The current version of the rtFlux utility only provides mass flow results, but the user can manually convert mass flow to mass flux based on the area of the "flux plane" (or cross sectional area of individual cells if such resolution is desired). Equations are presented in this section for mass flow, mass flux, and the cumulative mass passing through a plane.

Equations 1 and 2 describe the mass flow and mass flux, respectively, for the portion of a plane that intersects a single grid cell. Generic units are shown using mass (M), length (L), and time (T). The total mass to pass through the cross sectional area of a single grid cell for an incremental time is calculated as the average mass flow rate times the time period (Equation 3).

$$\text{Mass Flow Rate for the } p^{\text{th}} \text{ grid cell} = \dot{m}_{t,p} = C_{t,p} \cdot Q_{i,t,p} \quad [=] \frac{\text{M}}{\text{T}} \quad (1)$$

$$\text{Mass Flux for the } p^{\text{th}} \text{ grid cell} = J_{t,p} = \frac{\dot{m}_{t,p}}{A_{CS,p}} \quad [=] \frac{\text{M}}{\text{T} \cdot \text{L}^2} \quad (2)$$

$$\begin{aligned} &\text{Incremental Mass Passing Through} \\ &\text{the Plane in the } p^{\text{th}} \text{ Grid Cell} \\ &\text{Over an Incremental Time} \end{aligned} = \Delta m_{t,p} = \frac{1}{2} \cdot (\dot{m}_{t,p} - \dot{m}_{t-1,p}) \cdot (T_t - T_{t-1}) \quad [=] \text{M} \quad (3)$$

In these equations, $C_{t,p}$ is the concentration at the t^{th} transport time step for the p^{th} grid cell, $Q_{i,t,p}$ is the volumetric flow rate of the groundwater along the i^{th} axis (X, Y, or Z – whichever is of interest) at the t^{th} transport time step for the p^{th} grid cell, $A_{CS,p}$ is the (saturated) cross sectional area for the p^{th} grid cell, and T_t is the elapsed time at the t^{th} transport time step. These equations apply to a single cell based on the concentrations, volumetric flow rates, and cross sectional areas at the cell center. The concentrations are output from the RT3D simulation and the volumetric flow rates are read from the MODFLOW LKMT Package output file.

Equations 4 to 6 provide overall/average values for an entire plane comprised of N_{cell} grid cells having a total cross sectional area of $A_{CS, \text{plane}}$. Figure 9 depicts the combination of volumetric flow (arrow size) and concentration (color of the boxes) to determine mass flow (thickness of the boxes) for several grid cells and how this information is averaged to produce the result for a plane.

$$\text{Total Mass Flow Rate for Plane} = \dot{m}_{plane,t} = \sum_{p=1}^{N_{cell}} \dot{m}_{t,p} \quad [=] \frac{M}{T} \quad (4)$$

$$\text{Average Mass Flux for Plane} = J_{plane,t} = \frac{\dot{m}_{plane,t}}{A_{CS,plane}} \quad [=] \frac{M}{T \cdot L^2} \quad (5)$$

$$\begin{aligned} \text{Incremental Mass Passing} \\ \text{Through the Plane} \\ \text{Over an Incremental Time} \end{aligned} = \Delta m_t = \frac{1}{2} \cdot (\dot{m}_{plane,t} - \dot{m}_{plane,t-1}) \cdot (T_t - T_{t-1}) \quad [=] M \quad (6)$$

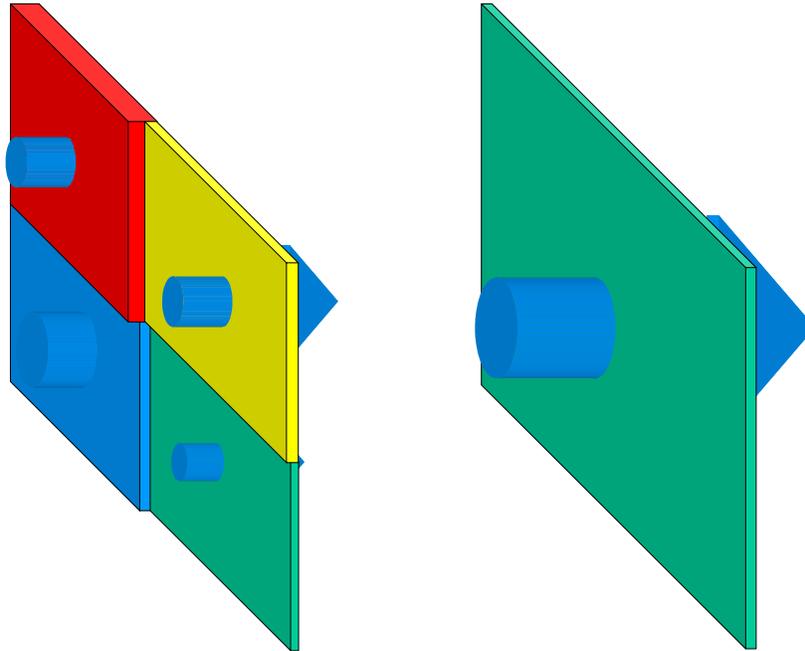


Figure 9. *Depiction of Mass Flow Through the Grid Cells That Comprise an Entire Plane — The total mass to pass across the plane of a grid cell (depicted by the thickness of the boxes) may vary because of differences in volumetric flow rate (size of arrows) resulting from aquifer heterogeneity and/or hydraulic stresses and differences in concentration (color of boxes with red = high, blue = low).*

5.0 Example Usage

5.1 Simple Example

A simple example application of the rtFlux software utility is presented here. The scenario involves a contaminant "spill" in a homogenous aquifer (represented by a single model layer) with a uniform gradient, as shown in Figure 10. The contaminant (e.g., vinyl chloride) undergoes aerobic degradation by aerobic direct metabolism. Thus, there are two chemical species (contaminant and oxygen) for RT3D to track. The simulation model is a single layer grid with 51 cells in the X direction and 31 cells in the Y direction. For this example four flux planes were specified in the X and Y directions as show in Figure 11. Figure 12 shows the plane definitions for these four flux planes. Figures 13 to 15 show standard RT3D results. The resulting concentrations of contaminant and oxygen after 730 days of the simulation are shown in Figures 13 and 14, respectively. Figure 15 shows time series plots for the concentrations of contaminant and oxygen at the observation location. Figures 16 through 19 show plots of the contaminant mass flow over time for planes 1 through 4, respectively, after post processing with the rtFlux utility. Figures 20 through 23 show plots of the oxygen mass flow over time for planes 1 through 4, respectively.

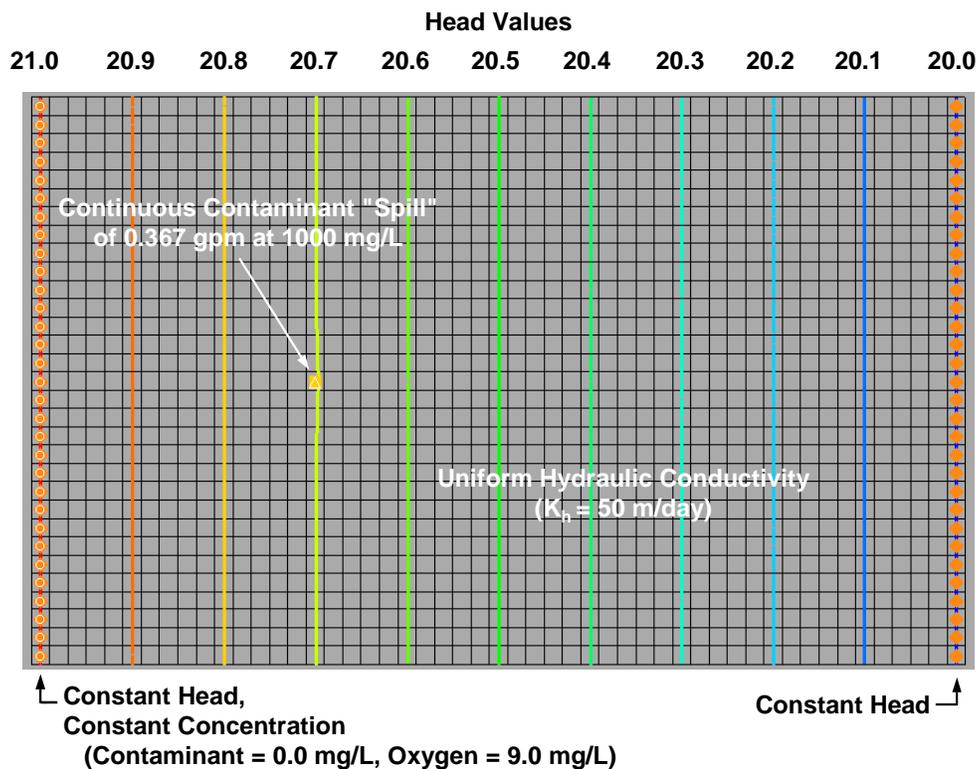


Figure 10. The Scenario for the Simple Example Showing the Uniform Hydraulic Gradient, Boundary Conditions, and the "Spill" Location

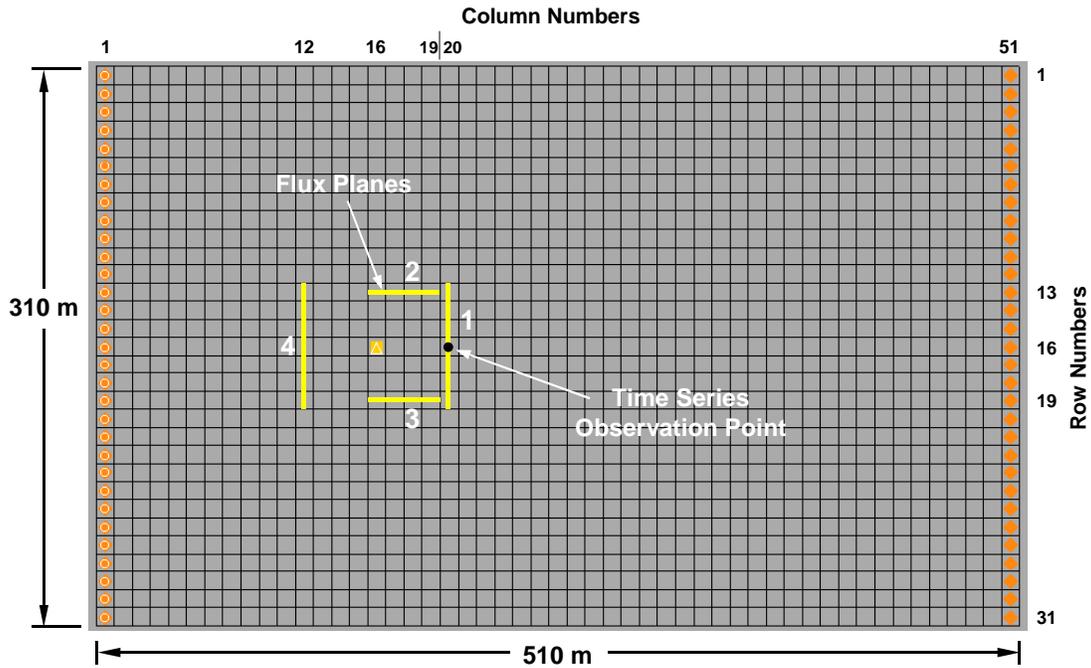


Figure 11. Locations of the Four Flux Planes Used in the Simple Example and the Observation Point for Time Series Concentration Plots

NCOL:	51
NROW:	31
NLAY:	1
Number of Planes:	4

BTN File:	
RT3D Superfile:	
LMKT Output File:	
IOB File:	

Plane Identifier	Upper Left Corner Cell			Opposing Corner Cell			Group ID	Plane Type
	COL	ROW	LAY	COL	ROW	LAY		
	20	19	1	20	13	1	1	YZ
	16	13	1	19	13	1	2	XZ
	16	20	1	19	20	1	3	XZ
	12	13	1	12	19	1	4	YZ

Figure 12. Plane Definitions For The Planes Shown In Figure 11

Contaminant After 730 Days

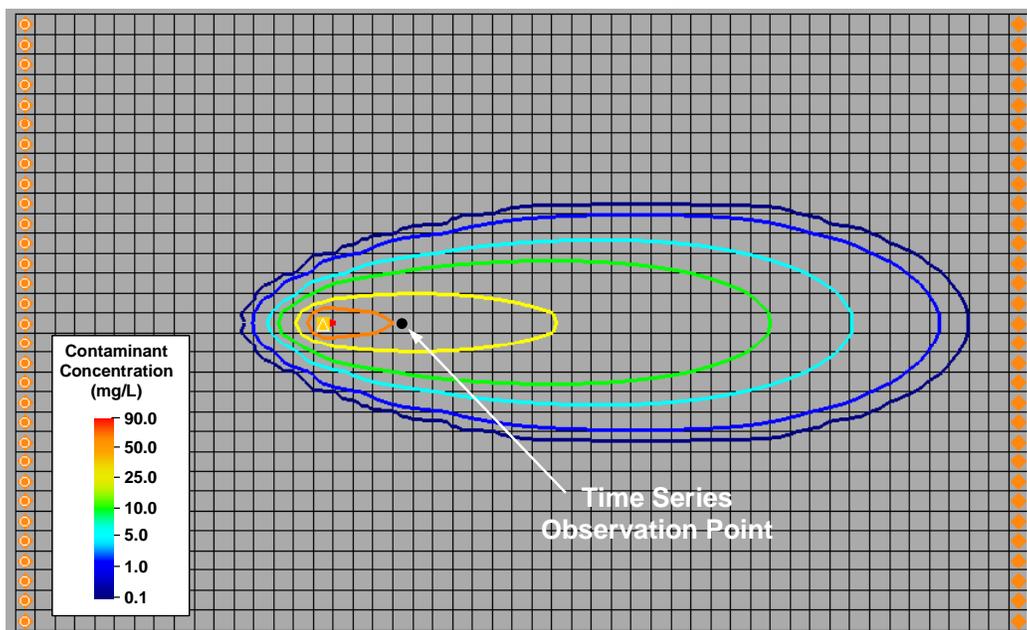


Figure 13. Concentration Contours After 730 Days for the Contaminant Component

Oxygen After 730 Days

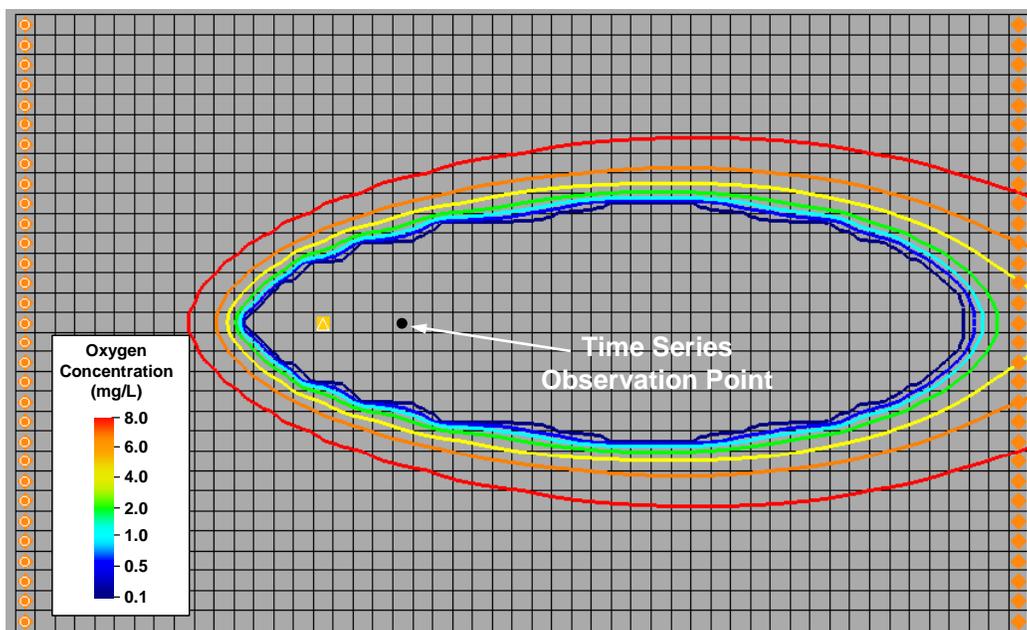


Figure 14. Concentration Contours After 730 Days for the Oxygen Component

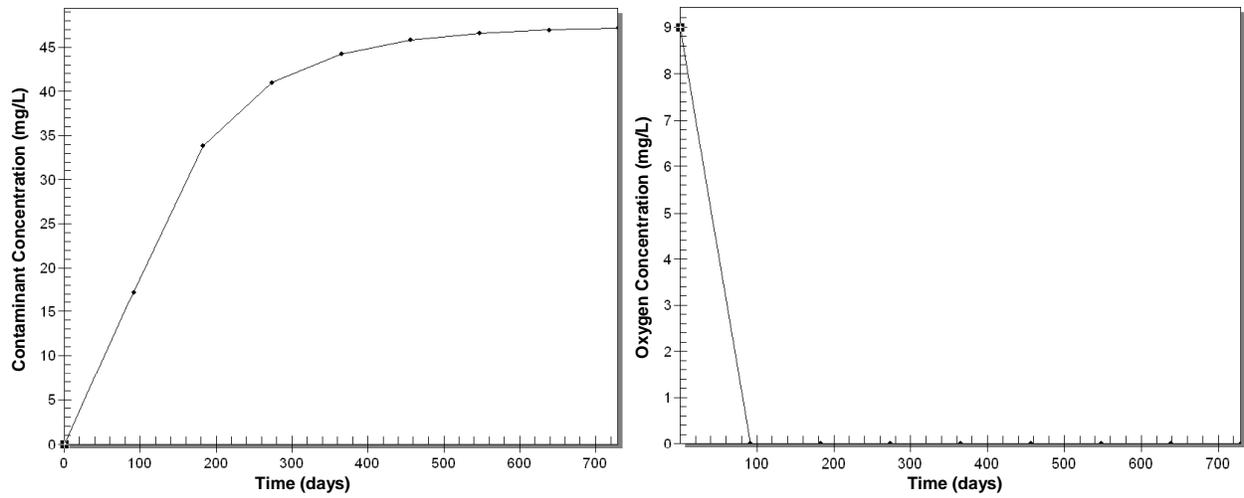


Figure 15. Time Series Data Plots for Contaminant and Oxygen Concentrations at the Observation Point

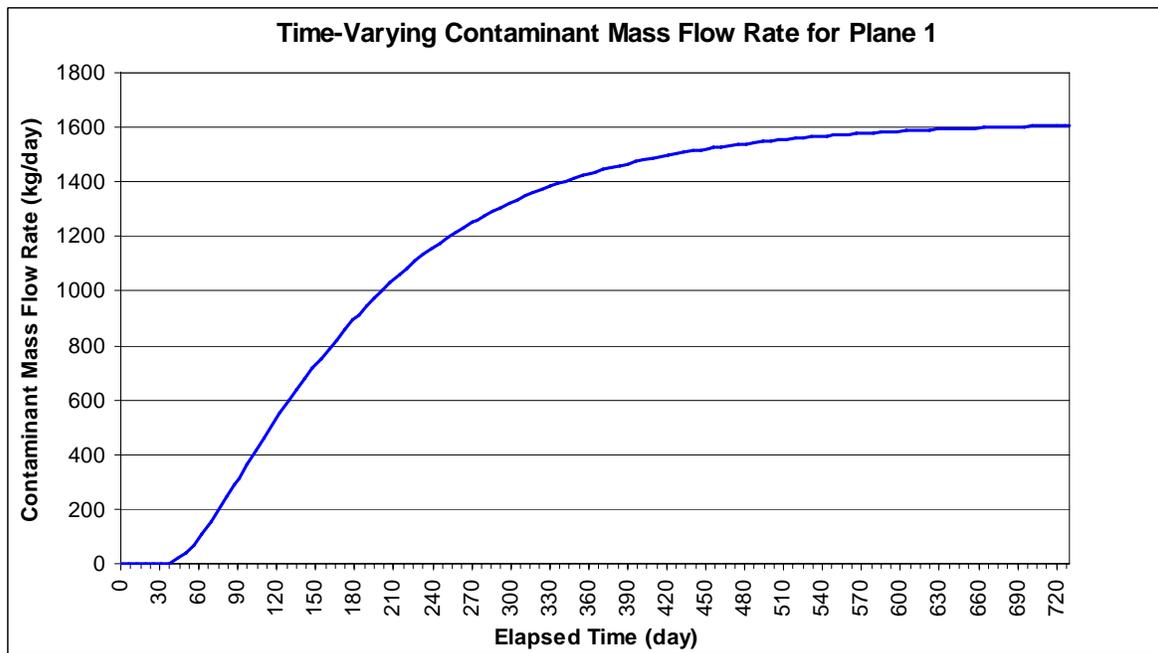


Figure 16. Plot of the Mass Flow Rate of Contaminant Across Plane #1 as a Function of Time

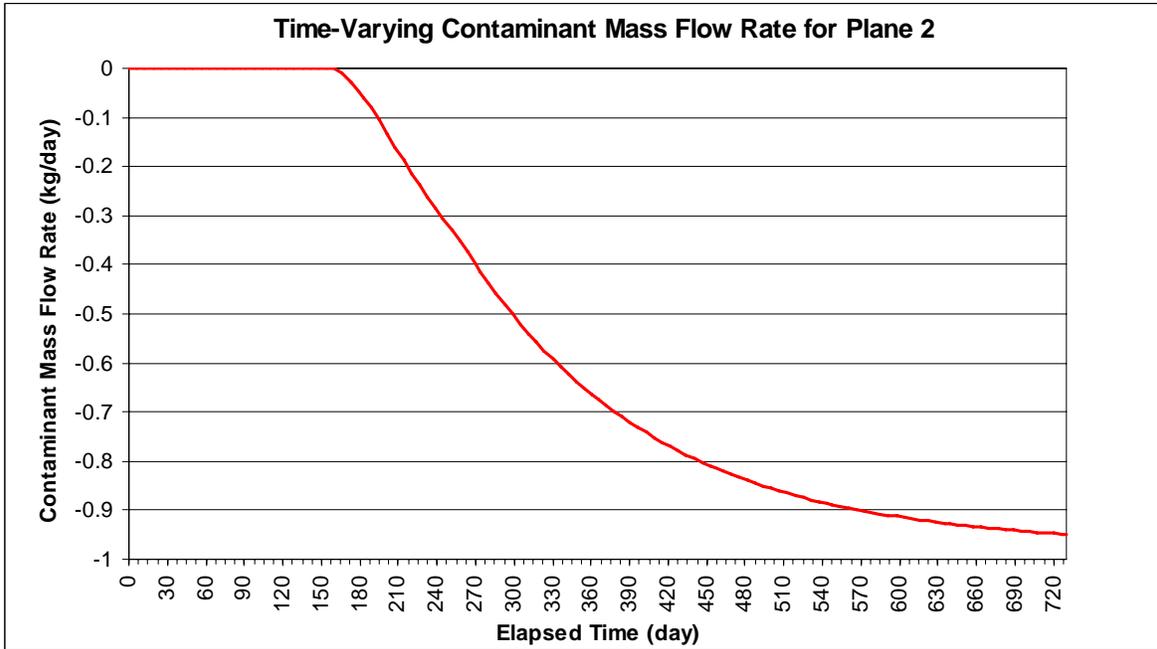


Figure 17. Plot of the Mass Flow Rate of Contaminant Across Plane #2 as a Function of Time

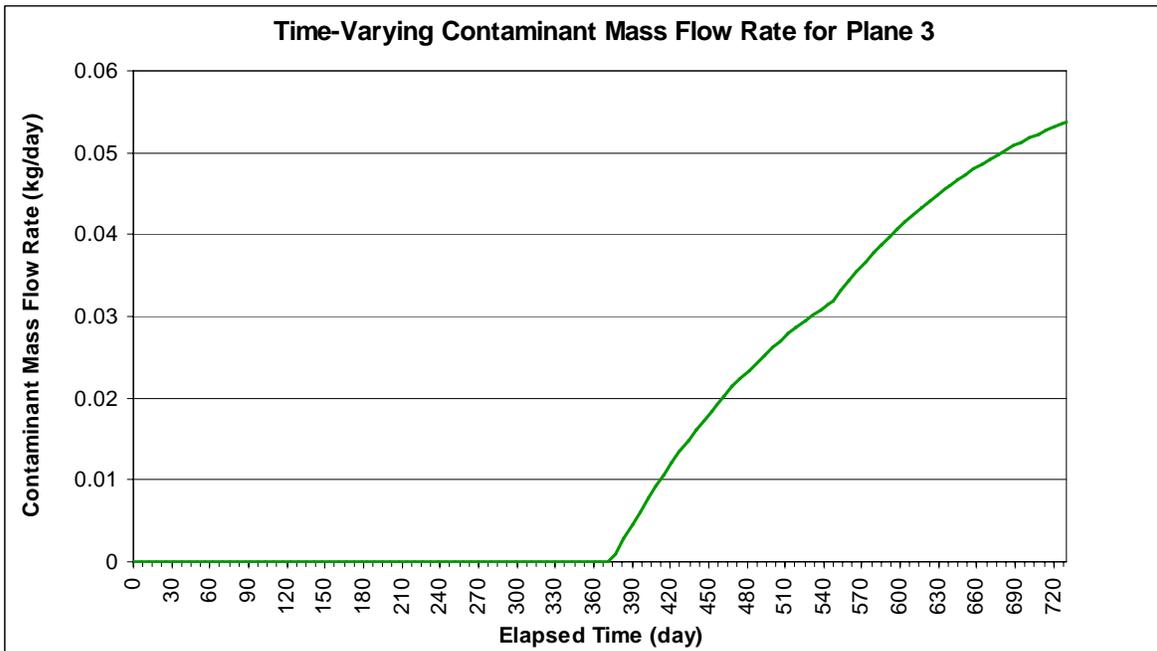


Figure 18. Plot of the Mass Flow Rate of Contaminant Across Plane #3 as a Function of Time

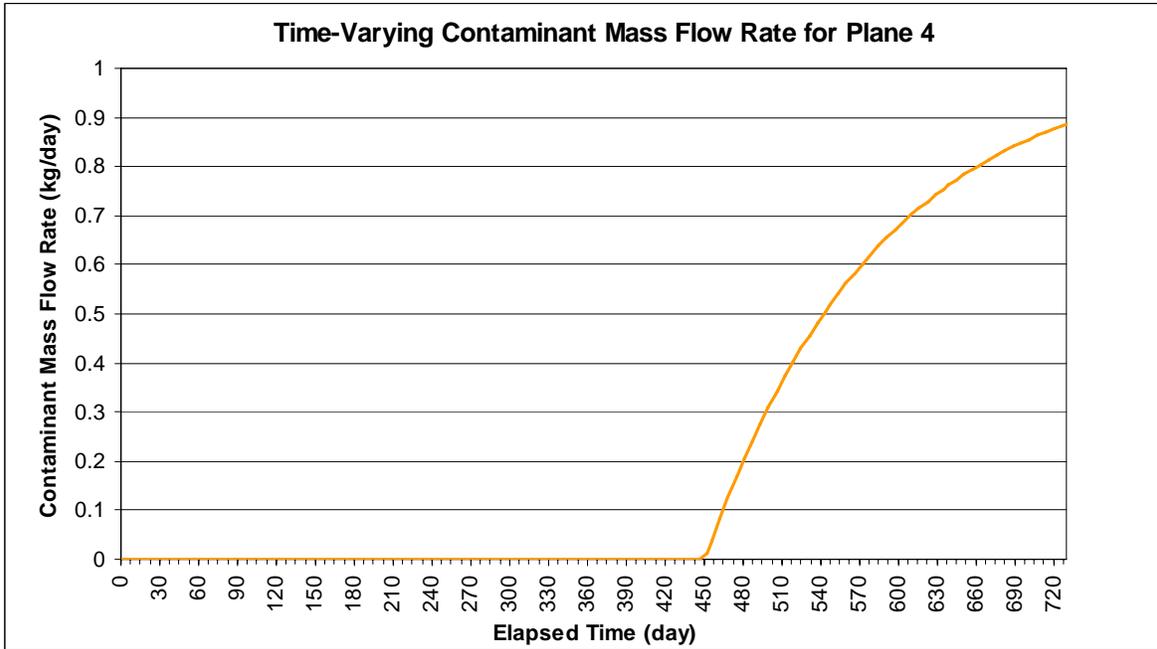


Figure 19. Plot of the Mass Flow Rate of Contaminant Across Plane #4 as a Function of Time

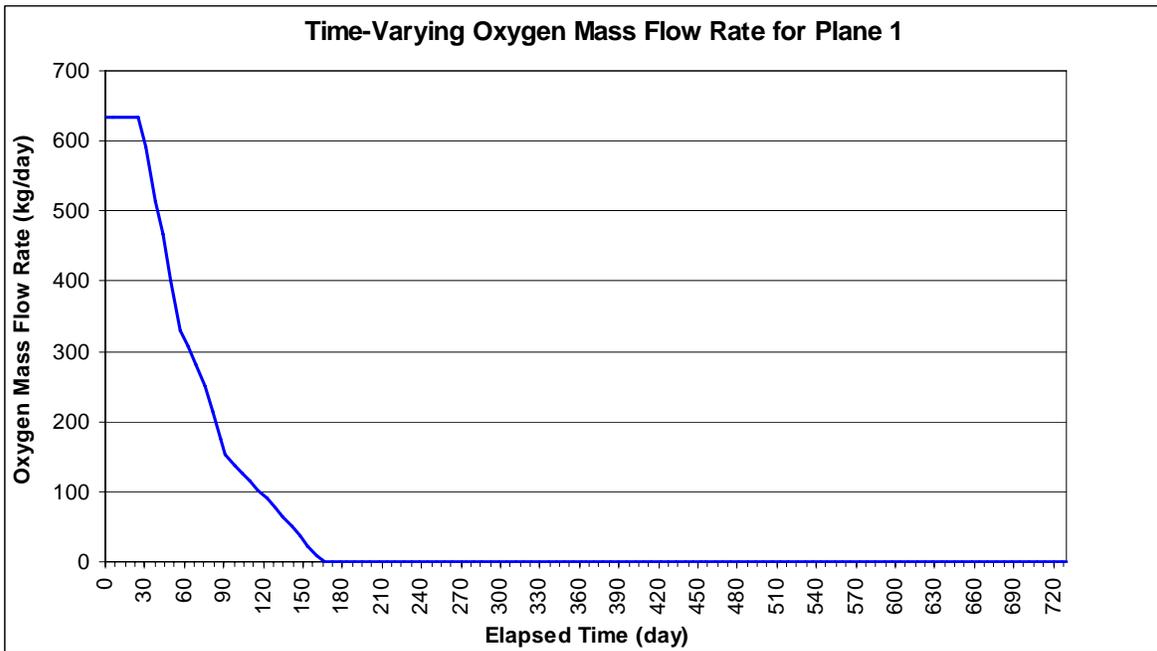


Figure 20. Plot of the Mass Flow Rate of Oxygen Across Plane #1 as a Function of Time

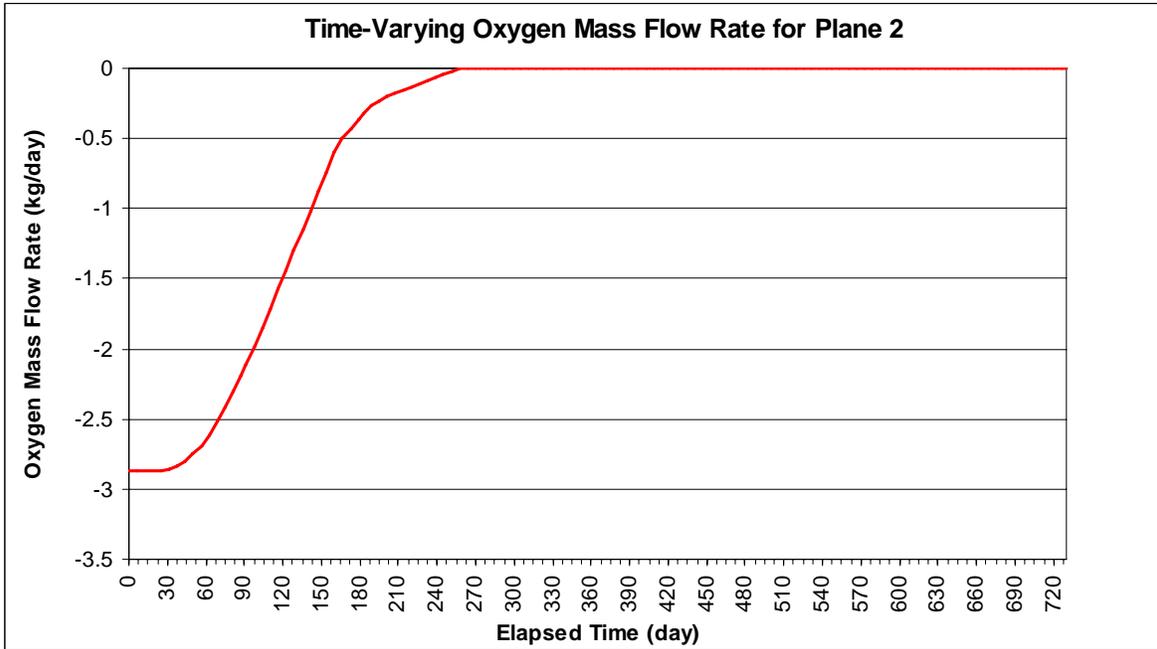


Figure 21. Plot of the Mass Flow Rate of Oxygen Across Plane #2 as a Function of Time

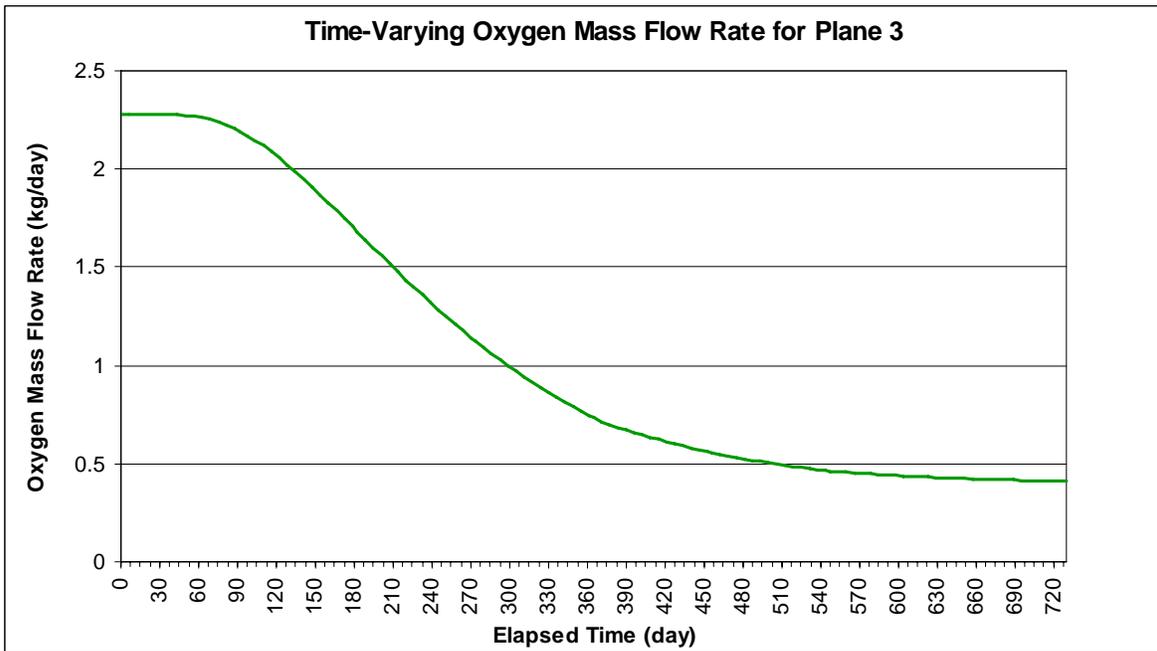


Figure 22. Plot of the Mass Flow Rate of Oxygen Across Plane #3 as a Function of Time

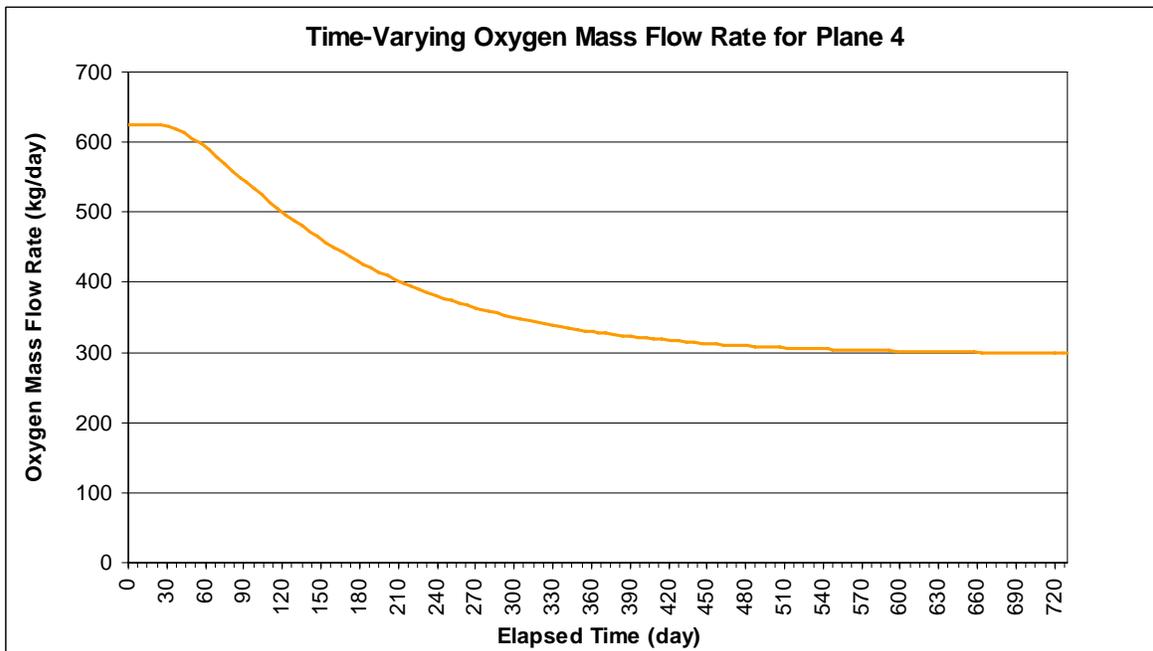


Figure 23. Plot of the Mass Flow Rate of Oxygen Across Plane #4 as a Function of Time

5.2 Multilayer Example

The simple example looked at the typical RT3D output, the configuration of flux planes, and the time series plots for mass flow. The multilayer example discussed in this section is more interesting with respect to the distribution of mass flow within the plane.

In this example, a rather large model is used to assess remediation scenarios for a single contaminant. The source area for the site has been removed, but a dissolved phase plume remains and is migrating downgradient towards receptors (Figure 24). Two simulations compare the results of natural attenuation processes (no active remediation) to the scenario of installing a pump-and-treat (P&T) system to intercept the bulk of the contaminant plume. The P&T system is operated for 25.5 years, then the residual plume is allowed to naturally attenuate. Several planes are defined (Figure 25), but plane #1 (located just downgradient of the P&T system) is of most interest for this comparison. The two scenarios were simulated using RT3D and the results were processed with the rtFlux utility. Figure 26 shows the mass flow rate and cumulative mass over time for plane #1. In the first scenario (no action) the mass flow through the plane is seen to increase as the core of the plume passes by the plane and then decrease because the contaminant source has been removed. In the second case, the P&T system effectively captures the dissolved contaminant plume, with the mass flow through the plane being about 15 times less than the "no action" scenario. When P&T is discontinued, the mass flow downgradient through the flux plane resumes. The cumulative mass plots are functions of the mass flow through the plane over time. For reference, contaminant contours for both scenarios are shown in Figure 27 at year 25.5.

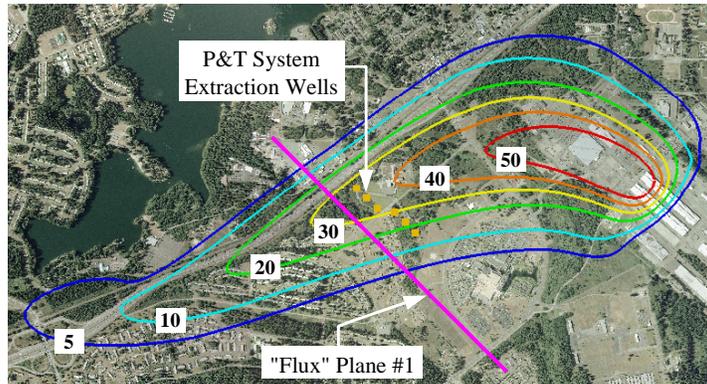


Figure 24. Plan View of the Multilayer Example Showing Initial Conditions in Layer 33, the Location of Flux Plane #1, and the P&T Wells

NCOL:	293	BTN File:	
NROW:	216	RT3D Superfile:	
NLAY:	46	LMKT Output File:	
Number of Planes:	5	IOB File:	

Plane Identifier	Upper Left Corner Cell			Opposing Corner Cell			Group ID	Plane Type
	COL	ROW	LAY	COL	ROW	LAY		
123	137	27	190	137	46	1	XZ	
109	166	28	109	193	46	2	YZ	
224	68	1	224	125	15	3	YZ	
196	68	1	196	125	15	4	YZ	
152	68	1	152	125	25	5	YZ	

Figure 25. Definition of the Planes for the Multilayer Example

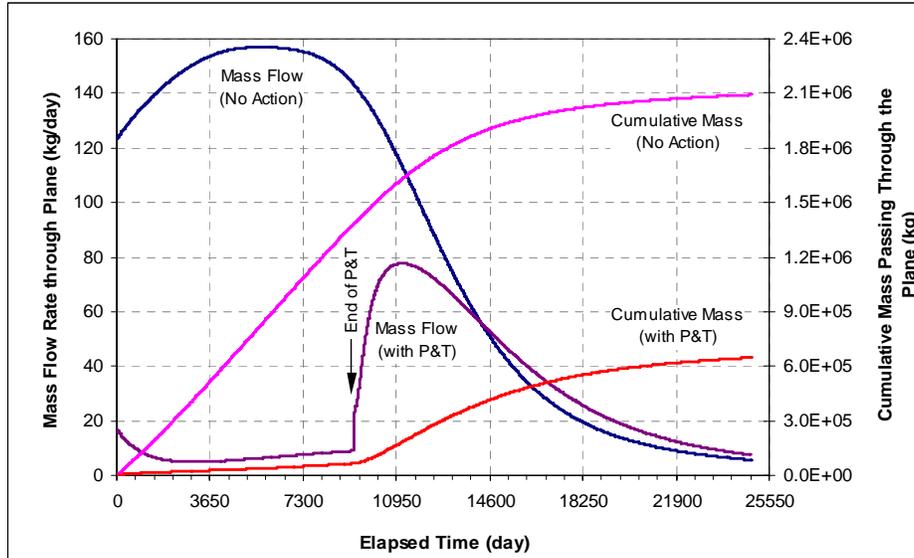


Figure 26. Mass Flow Rate and Cumulative Mass to Pass Through a Plane for the Two Scenarios of the Multilayer Example — In one case no action is taken (natural attenuation only) and in the other P&T is applied. In both cases, the non-aqueous phase liquid source was removed.



Figure 27. Contaminant Contours ($\mu\text{g/L}$) After 25.5 Years for the Scenarios of (A) Natural Attenuation Only and (B) Pump-And-Treat; the Pump-And-Treat System Was Discontinued After this Time

Data for bubble plots are available at regular time intervals. As an example, Figures 28 to 30 show the bubble plots of the volumetric flow rate, contaminant concentration, and mass flow rate, respectively, at an elapsed time of 10000 days (~27 years) in plane #1 for the natural attenuation only scenario. The displayed extent of plane #1 has been cropped to just beyond the extent of the plume for presentation purposes. Above layer 31 there is a clay confining layer, which is apparent from the grid cells with much smaller or no bubbles for volumetric flow (Figure 28). A similar low conductivity zone exists in the bottom layers. The volumetric flow is

relatively uniform within each of several zones of differing hydraulic conductivity. The contaminant concentration (Figure 29) is distributed laterally around a high concentration core near the center of the flux plane. The mass flow (Figure 30) is the product of the volumetric flow rate and the concentration, thus exhibits a distribution with the highest mass flows at the points of high concentration and high volumetric flow rate.

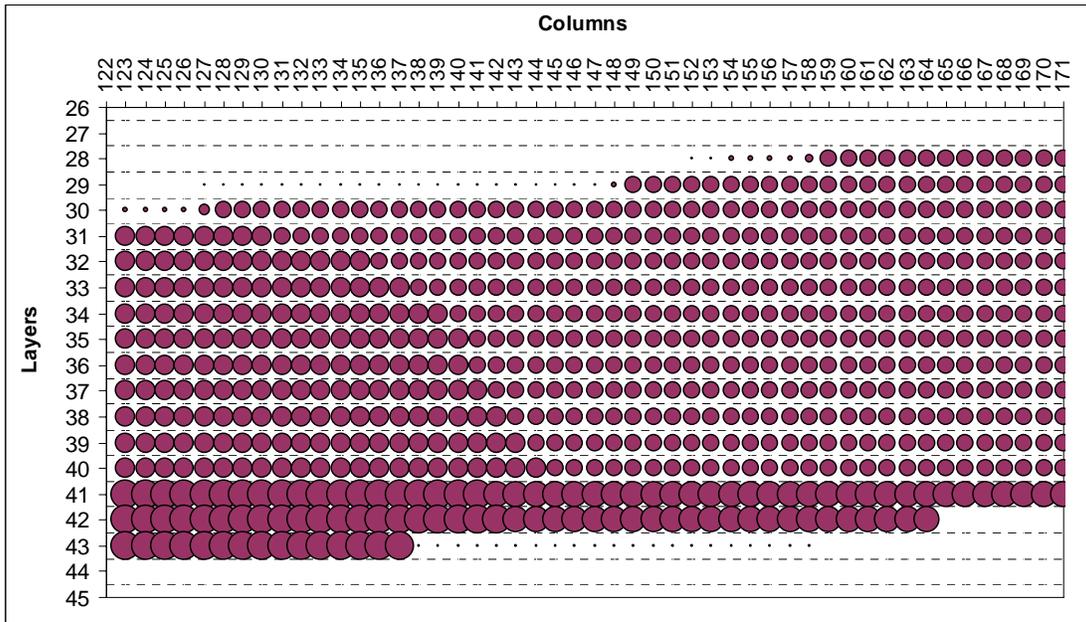


Figure 28. *Relative Volumetric Flow Rate (e.g., ft³/day) at Flux Plane #1 on Simulation Day 10000 of the Multilayer Example "No Action" Scenario*

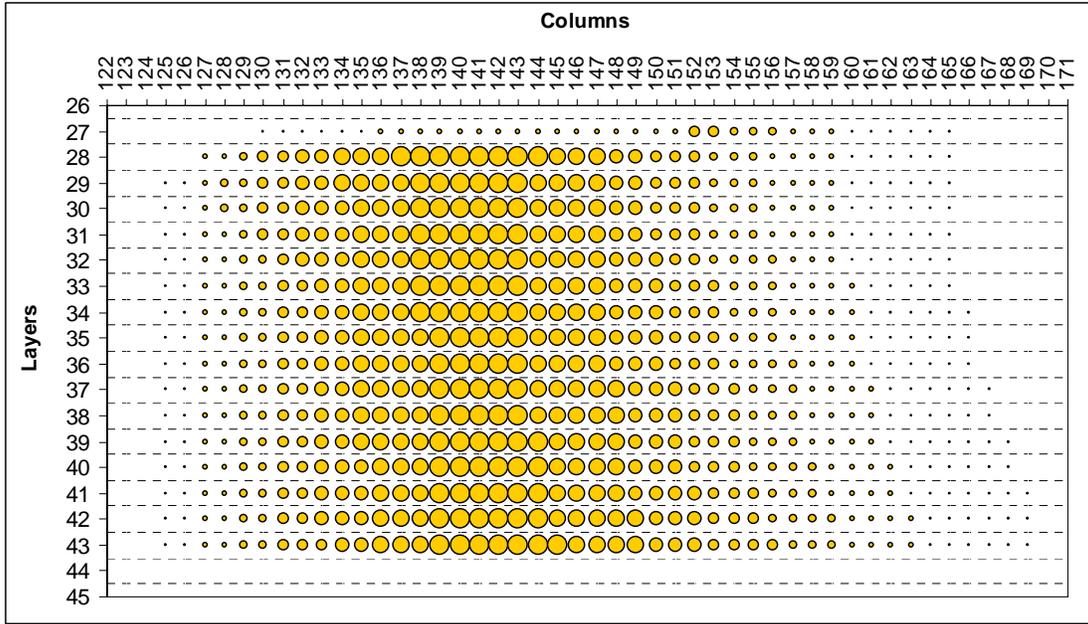


Figure 29. *Relative Contaminant Concentration (mg/L) at Flux Plane #1 on Simulation Day 10000 of the Multilayer Example "No Action" Scenario*

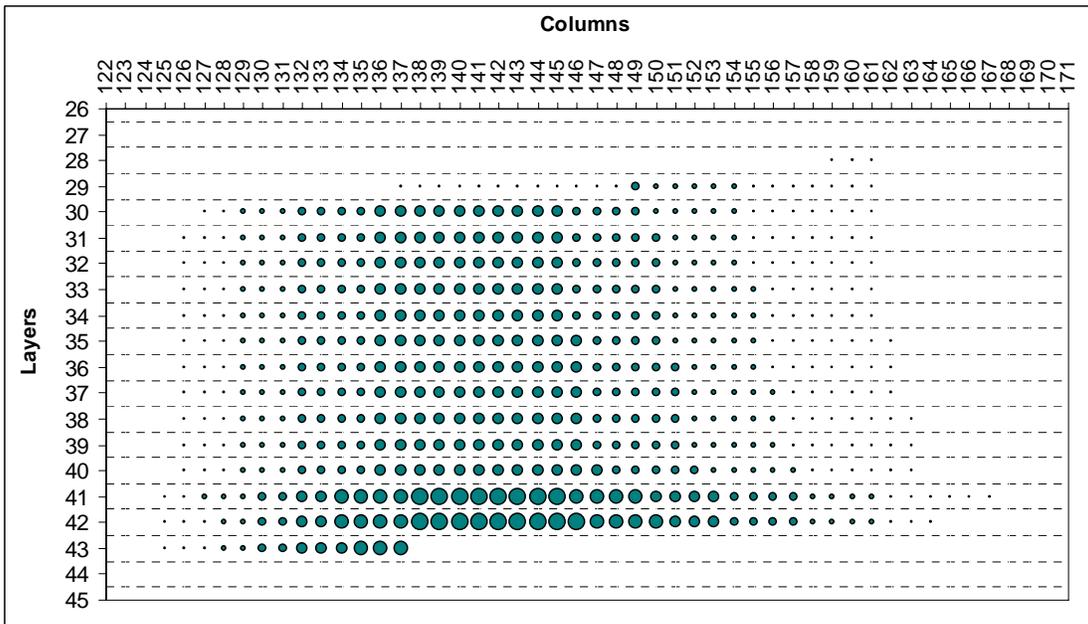


Figure 30. *Relative Mass Flow Rate (kg/day) at Flux Plane #1 on Simulation Day 10000 of the Multilayer Example "No Action" Scenario*

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